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Fundamental Science and Structural Applications Covered in Area of  
Nanomaterials  
(See MRS Proceedings Volume 740)

Symposium I on Nanomaterials for Structural Applications provided an overview of current multidisciplinary research in this rapidly growing field with the primary focus of reinforcing the relationship between basic science and engineering at the nanoscale level. Thematic sessions covered nanostructured bulk materials, films, coatings, and nanocomposites. These new materials are now being introduced in structural applications, such as wear resistance and plastic-forming, and load-bearing uses. Nanophase or nanocrystalline materials are also being used in electronics, refractory, biological, and catalytic applications. Progress in a wide range of structural applications for nanomaterials crucially depends on the development of new fabrication and processing technologies, along with a fundamental understanding of the relationship between the structure and properties.

Among the most important issues discussed are experimental data, and theoretical and computer models concerning deformation mechanisms in nanostructured materials, which, in general, are different from those in conventional coarse-grained materials. The competition between conventional and unusual deformation modes is believed to cause the unique mechanical properties of nanomaterials, serving as a basis for their structural applications. Fabrication of nanomaterials with bimodal (nano- and micrograined) composite structures, that exhibit both very high strength and reasonable ductility, represents a promising strategy in synthesis of nanomaterials with enhanced mechanical characteristics for various applications. High strain rate and low-temperature super plasticity of some nanocrystalline materials are the subjects of growing fundamental research efforts motivated by a range of new applications of these super strong and super plastic materials in net shaping technologies.

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**SYMPOSIUM I**  
**Nanomaterials for Structural Applications**

December 2 - 6, 2002

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## SESSION II: FRACTURE AND MECHANICAL PROPERTIES - I

Chairs: Asiru Vasudevan and Amiya K. Mukherjee  
Monday Morning, December 2, 2002  
Room 312 (Hynes).

### 8:30 AM \*I1.1 DEFORMATION AND COBLE CREEP OF NANOCRYSTALLINE MATERIALS. C.S. Pande and R.A. Masumura, Materials Science and Technology Division, Naval Research Laboratory, Washington, DC.

Modeling of strengthening by nanocrystalline materials need consideration of dislocation interactions and sliding due to Coble Creep, both of which may be acting simultaneously. Such a mechanism is considered in this paper. It is shown that a model based on using Coble creep (with a threshold stress) for finer grains and conventional Hall-Petch strengthening for larger grains, appears to be most successful in explaining experimental results provided care is taken to incorporate into the analysis the effect of grain size distribution occurring in most specimens. Use of an alternate formalism of Coble Creep proposed recently gives a somewhat less satisfactory agreement with experiments.

### 9:00 AM I1.2 RATE DEPENDENT DEFORMATION AND FAILURE IN NANOCRYSTALLINE MATERIALS. M. Dao, N. Chollacoop, Y.-N. Kwon and S. Suresh, Dept of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Tensile experiments on high-purity, nearly defect-free electrodeposited nanocrystalline Ni samples have shown that an abnormal strain rate dependent tensile behavior exists, i.e., both strain-to-failure and the failure stress increased significantly with increased loading rates. Similar trends have been reported in the literature for nanocrystalline pure Cu and certain Al-Fe alloys. Exploiting recent computational simulation results and TEM observations of nanocrystalline materials, a simple computational model is proposed assuming distinctively different plastic deformation characteristics between the grain interior (where the plastic deformation is much harder due to the lack of dislocation sources) and the Grain Boundary Affected Zone (GBAZ) near grain boundary area (where the plastic deformation is much easier due to the presence of nearby grain boundaries). The plastic deformation within the GBAZ is treated as rate-dependent and a strain-based failure/damage criterion is assumed. The proposed model captures the trends in terms of strain-to-failure and the failure stress very well. The strain-rate dependent strengthening effect of GBAZ at increased strain rates is suggested to be a most important factor in delaying the macroscopic failure according to the computational results. A parametric study of the effects of key mechanical and structural variables on the rate dependence of deformation is also carried out.

### 9:15 AM I1.3 STRAIN INDUCED ELASTOMER BUCKLING INSTABILITY FOR MECHANICAL MEASUREMENTS (SIEBIMM). Christopher M. Stafford, Christopher Harrison, Alamgir Karim, and Eric J. Amis, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD.

We introduce a new technique (SIEBIMM) for high-throughput measurements of the mechanical properties of thin polymeric films. This technique relies upon a highly periodic strain-induced buckling instability that arises from a mismatch of the moduli of a relatively stiff polymer coating on a soft silicone sheet. The modulus-dependent buckling wavelength, typically 1-10 microns for 100 nm thick glassy films, is rapidly measured by conventional light scattering. The SIEBIMM-measured modulus is shown to agree with that measured by conventional Instron-like techniques. We directly show that the buckling instability is highly sinusoidal at low strain (first order diffraction peak is ten times higher in intensity than second order) thereby insuring the suitability of simple mechanical analysis. Utilizing our expertise in preparing thickness gradients via flow coating, we demonstrate that the flexural rigidities of thin films having a wide range of thicknesses can be measured in minutes. By measuring the temporal decay of strain-induced diffraction peaks for plasticized coatings we show that this technique can evaluate viscoelastic properties, such as creep. We also show that a large amount of strain induces cracking in films, resulting in an optical signature where the scattering intensity decays smoothly with wavenumber. We demonstrate SIEBIMMs capability with several academic and industrially-relevant polymeric systems, including polystyrene loaded with a wide range of plasticizer, blend of block copolymers with polystyrene and polyisoprene blocks (Vector 4215 and 4411), and a thiolene-based ultraviolet curing adhesive.

### 9:30 AM I1.4 TENSILE DEFORMATION AND FATIGUE CRACK GROWTH IN

### Al-7.5Mg BULK NANOCRYSTALLINE MATERIALS. P.S. Pao, H.N. Jones, S.J. Gill, and C.R. Feng, Naval Research Laboratory, Washington, DC.

The tensile deformation and fatigue-crack growth rates of bulk nanocrystalline Al-7.5Mg were investigated. Nanocrystalline particulates were first prepared by mechanically ball milling spay atomized Al-7.5Mg powders in liquid nitrogen. These particulates were then degassed, consolidated by hot isostatic pressing, and extruded into rods. Some extruded rods were subjected to further closed-die forging. The average grain size in the cryo-milled particulates is about 25 nm. Following elevated temperature degassing, HIP, and extrusion, however, the grains coarsened considerably to an average size of about 250 nm. The tensile and yield strengths of bulk nanocrystalline Al-7.5Mg are more than twice those of Al 5083-H321, while the tensile elongation of the nano alloy is significantly lower. The tensile fracture of the bulk nanocrystalline Al-7.5Mg is preceded by the apparent formation of shear banding. In contrast to the low dislocation activity in the undeformed matrix, the gage section and the shear band region both exhibited high dislocation density and dislocation cell structure. Fatigue crack growth rates of nanocrystalline Al-7.5Mg are significantly higher than those of ingot-processed 7050-T7451. The fatigue crack growth thresholds of the nanocrystalline Al-7.5Mg are significantly lower than that of 7050-T7451. The higher fatigue crack growth rates and lower thresholds may be attributed to the much smoother fracture surface morphology and lower roughness induced crack closure in bulk nanocrystalline Al-7.5Mg. The fracture toughness of the nanocrystalline Al-7.5Mg extrusions is significantly lower than those of nanocrystalline forgings, which in turn are lower than that of 7050-T7451. The reason for the lower fracture toughness in bulk nanocrystalline Al-7.5Mg alloys is not fully understood yet but may be related to the intense fiber texture present in the alloy.

### 9:45 AM I1.5 ANALYTIC PREDICTION OF HALL-PETCH EXPONENT IN MULTILAYER COATINGS. Lawrence H. Friedman, Pennsylvania State University, Dept of Engineering Science and Mechanics, State College, PA.

Elastically inhomogeneous multilayer films are being exploited for use as ultra-hard coatings. These films exhibit a strong dependence between the compositional wavelength of the film,  $\Lambda$ , and hardness. The Hall-Petch Relation, based on dislocation pileup theory, has been applied to explain and quantify experiments concerning this dependence. The original Hall-Petch Relation predicted variation of yield stress of a poly-granular solid with respect to the grain size to be  $\sigma_y = K \Lambda^{-1/2} + \sigma_0$ , where  $d$  is the average grain diameter and  $\sigma_0$  a constant "friction" stress. In the modern context of multilayer films, the Hall-Petch Relation requires modification due to the elastic inhomogeneity of the multilayer,  $\sigma_y = K \Lambda^{-a} + \sigma_0$  where the scaling exponent  $a$  depends on the elastic properties of the individual layers (Friedman and Chrzan, 1998). Although the the rationale and framework for this scaling behavior has been previously established, there was no general method to predict the actual exponent,  $a$ , except by numerical experiment (dislocation modelling). Here, the problem of predicting the scaling exponent is reduced to an easily solved eigenvalue problem, and the scaling exponent is predicted as a function of the elastic moduli, dislocation character (screw, edge or mixed) and pileup orientation.

### 10:30 AM \*I1.6 MEASURES OF INTERFACES IN NANOSTRUCTURES. G. Knöner, V. Barbe, K. Reimann, W. Sprengel, and H.-E. Schaefer, University of Stuttgart, Institut für Theoretische und Angewandte Physik, Stuttgart, GERMANY.

For the properties of nanostructured solids the high number of interfaces is of pivotal importance. In the present paper recent data on the temperature dependence of the atomic structure of interfaces in nanocrystalline materials obtained by positron annihilation will be discussed [1,2]. In addition, selfdiffusion studies in nanocrystalline pure materials [3], intermetallic FeNbB compounds [4] and  $n\text{-ZrO}_2\text{-Y}_2\text{O}_3$  ceramics [5] will be reported.

- [1] R. Würschum et al., Phys. Rev. B **62**, 12021 (2000)
- [2] L. Pasquini et al., Phys. Rev. B **63**, 134114 (2001)
- [3] H.-E. Schaefer et al., Mat. Sci. Eng. **A286**, 24 (2000)
- [4] V. Barbe, Diploma Thesis, Stuttgart University (2002)
- [5] G. Knöner, Diploma Thesis, Stuttgart University (2002)

### 11:00 AM I1.7 DEFORMATION OF CRYOMILLED NANOCRYSTALLINE Al-Mg ALLOY. Zonghoon Lee, Department of Materials Science, University of Southern California, Los Angeles, CA; Bing Q. Han, Farghali A. Mohamed, Enrique J. Lavernia, Department of Chemical and Biochemical Engineering and Materials Science, University of California at Irvine, Irvine, CA; and Steven Nutt, Department of Materials Science, University of Southern California, Los Angeles, CA.

The deformation of bulk nanocrystalline Al-Mg alloy was investigated using transmission electron microscopy and high-resolution electron microscopy. Grain refinement was achieved by cryomilling of elemental powders, and powders were consolidated by hot isostatic pressing (HIP) and extrusion to produce bulk nanocrystalline Al-Mg alloy. The microstructure of cryomilled Al-Mg alloy consisted of equiaxed and elongated grains with approximate size of 400 nm, which were elongated along the extrusion direction. The Al-Mg alloy exhibited unusual deformation characteristics involving complex interactions between nanocrystalline grains. Elongated grains were comprised of dislocation cells, sub-grains, and slip bands. Dislocation cells tended to be limited to a critical size, and sub-grain boundaries formed smaller grains inside the original grains, storing the energy of deformation. Grain partitioning was observed in severely deformed regions comprised of high-density dislocation cells. Nanocrystalline second phases were distributed inside the grains and grain boundaries. Investigation of bulk tensile fracture specimens revealed unusual failure mechanisms and interactions between nanocrystalline grains. Tensile behavior was characterized by high yield strength, high ductility, and low strain hardening. Strain rate had a negligible effect on the tensile behavior. After the yield point, the alloy exhibited nearly perfectly plastic behavior and low strain hardening. The relations between deformation mechanisms and mechanical behavior of the bulk nanocrystalline alloy are presented as well.

#### 11:15 AM I1.8

**HARDNESS AND ABRASION RESISTANCE OF NANO-CRYSTALLINE NICKEL ALLOYS NEAR THE HALL-PETCH BREAKDOWN REGIME.** C.A. Schuh and T.G. Nieh, Materials Science and Technology Division, Lawrence Livermore National Laboratory.

The breakdown of classical Hall-Petch scaling remains an area of scientific interest, and will govern the limiting strength of nanocrystalline alloys for structural applications. In this work we discuss the hardness and scratch resistance of nanocrystalline nickel and nickel-tungsten solid solution alloys, assessed through nanoindentation and nano-scratch techniques. The materials have been prepared by electrodeposition, and are fully dense with grain sizes between 4 and 22 nm. In this range of grain sizes, there is some evidence for a breakdown of Hall-Petch scaling, reflected in both the hardness and abrasion data. The role of solid solution alloying on this breakdown is also discussed.

#### 11:30 AM I1.9

**HYBRID NYLON-6/SILICA NANOCOMPOSITES WITH IMPROVED MECHANICAL PROPERTIES.** M.M.L. Garcia Curiel, W.E. van Zyl, and H. Verweij, Faculty of Chemical Technology and MESA Research Institute, University of Twente, Enschede, THE NETHERLANDS.

The study involves the development of new strategies to form technically interesting hybrid nanocomposites with improved mechanical properties. In particular, a new "dissolution" preparative route was developed which incorporates silica nanoparticles (<30 nm) into a nylon-6 matrix. The procedure relies on the judicious choice of organic solvent and pH control. The synthesis involves the dissolution of nylon-6 in formic acid followed by silica particle addition (as an acidified, monodisperse sol) with stirring. Viscous solutions were prepared under cleanroom conditions and casted as thin films which are dried and vacuum treated at ~60°C. The dried films were submitted for TEM analysis after microtoming the samples. TEM images revealed that the silica particles i.) retained their original shape and size (10-30 nm), ii.) are mono-dispersed and iii.) mainly non-agglomerated. The degree of crystallinity of the composites was determined with XRD as a function of percentage filler added. The nylon-6 phase is semi-crystalline while the silica phase is amorphous. Initial mechanical tests on the composites were conducted and showed with 1wt% silica addition, an increase in toughness and E modulus can be observed. The increase in mechanical properties may be a result of the nanosize filler particles which has good synergy with the nylon matrix. See preliminary communication: *Macromol. Mater. Eng.*, 2002, 287, 106.

#### SESSION I2: FRACTURE AND MECHANICAL PROPERTIES - II

Chairs: Lawrence Kabacoff and Hans-Eckhardt Schaefer  
Monday Afternoon, December 2, 2002  
Room 312 (Hynes)

#### 1:30 PM \*I2.1

**NANOSTRUCTURED MATERIALS AND THE SIZE-DEPENDENCE OF PROPERTIES.** Subra Suresh, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

Experimental and computational results on the size dependence of properties will be addressed with particular reference to nanostructured materials. The experiments will include ex-situ observations of deformation, damage evolution and failure in nanocrystalline materials synthesized by recourse to a variety of different processing techniques. Observations of these phenomena gathered during the mechanical test by means of high-resolution transmission electron microscopy as well as two-dimensional experimental analogues involving the bubble raft model will also be presented. These experimental results will then be used to guide very detailed computational simulations of mechanical response wherein multiple length scales spanning the atomistic to the continuum levels will be considered. Issues and challenges in the understanding of complex phenomena such as fatigue failure and tribological damage evolution will also be briefly addressed.

#### 2:00 PM I2.2

**FATIGUE AND FRACTURE BEHAVIOR OF NANOSTRUCTURED NICKEL.** T.A. Venkatesh and S. Suresh, Dept. of Materials Science and Engineering, MIT, Cambridge, MA.

Nanostructured materials with their high strength, superior hardness, and enhanced wear resistance characteristics, have been studied extensively over the past two decades. While some insights have been obtained towards understanding the basic deformation mechanisms in metallic and ceramic nanostructured materials, very little is known about their fatigue and fracture characteristics. Choosing electrodeposited nanocrystalline nickel as a model system, comprehensive and systematic series of experiments have been performed to characterize total fatigue life, fatigue threshold, and fracture toughness as a function of various microstructural and mechanical variables such as the grain-size (20-200 nm) and R-ratio. Values of endurance limit for stress-controlled fatigue, subcritical fatigue crack growth resistance as well as the critical stress intensity factor for the onset of quasi-static fracture for the ultrafine-grained nickel are compared with the corresponding values for microcrystalline nickel. Furthermore, through high-resolution SEM and TEM microscopy observations, key features of the fatigue and fracture characteristics such as striations and void formation will be discussed within the context of the observed fatigue behavior of the micro-grained nickel alloys.

#### 2:15 PM I2.3

**MECHANICS OF NANOSTRUCTURES.** Rod Ruoff, Northwestern University, Evanston, IL.

We have developed new tools for measuring the mechanical response of nanoscale specimens that could play a role in many applications that would benefit from their mechanical properties. Our concentration has been on carbon nanotubes, but recently we measured the mechanical resonance response of various types of nanofilaments, including of amorphous  $\text{SiO}_2$  and amorphous B nanowires. In this talk I will discuss how these testing stages work, and describe some measured properties of such nanostructures: response to tensile loading, nanotribology, and mechanical resonance behaviour. Support is appreciated from the NASA Langley Research Center Computational Materials: Nanotechnology Modeling and Simulation Program, the ONR MIS program (previous), and the NSF NIRT program.

#### 2:30 PM I2.4

**THE DEPENDENCE OF INDENTATION CRACKING IN SILICON CARBIDE ON INDENTATION SPACING.** R. Sarrabi-Nour, L. Tsakalakos, and M. Manoharan, GE Global Research Center, Niskayuna, NY.

The issue of multiple cracks in materials and their interaction is central in understanding the overall fracture behaviour of materials. Indentation cracking has been extensively used for the measurement of fracture toughness due to its small sample size requirements as well as a relatively good correlation with values obtained from traditional fracture mechanics tests. The majority of these studies have focused on the fracture behaviour of a single indent. The present study was aimed at understanding the effect of interaction between the cracks generated on SiC from a pair of sequential indents. These were done both at the micro and nano scales, with the nano scale studies being done with a nanoindenter. The distance between the indents was varied from a level comparable to the crack size to a level where interaction could be ignored. This paper discusses the changes in the nature as well as the sizes of cracks due to interaction between the stress fields of the indents. This information is potentially useful in determining damage interaction in nanomaterials.

#### 2:45 PM I2.5

**INFLUENCE ON AN ELECTROCHEMICALLY GENERATED NANOTOPOGRAPHY ON WEAR, CORROSION, AND FATIGUE OF AUSTENITIC STAINLESS STEELS.** Robin Büscher, Ilia

Tikhovski, Anna Runiewicz, and Alfons Fischer, Werkstofftechnik, Universitaet Essen, Essen, GERMANY.

In many technical and medical tribological systems there is a need for surfaces, which have to undergo contact pressures in combination with a chemical attack without generating too much wear loss. In MEMS and NEMS devices there is an urgent need for extremely low wear rates, because of the small size of the components. They do not allow for a high run-in wear rate as it is mostly the case before steady-state is reached. In medical applications like artificial metallic hip joints is known that particles will provoke foreign-body reactions in the surrounding tissue, which are detrimental for the performance of the entire implant. Many attempts to improve the properties of surfaces have been carried out. Some make use of organic or inorganic coatings by CVD, PVD, electrochemistry, etc, while others change the mechanical and chemical properties of existing surfaces by ion-implantation, diffusion etc. Another possibility is to change the surface topography by mechanical (e.g. stamping), physical (e.g. laser) or chemical (e.g. etching) procedures. Thus, the beneficial effect of just changing the topography in a  $\mu\text{m}$ - to nm-scale has been shown already [1]. The weight loss after 1 km wear path could be lowered by a factor of 14, while particles of approximately 10 to 500 nm size were generated. This contribution investigates how the corrosion as well as the fatigue behaviour is influenced by the changes in surface topography. Due to the fact that corrosion is solely and fatigue distinctly influenced by surface properties it is crucial for the performance of products that these properties do not deteriorate, distinctly. Corrosion is tested by polarization curves in 1% NaCl solution while the fatigue behaviour is examined by rotating bending within the same surrounding medium. The wear, corrosion, and fatigue behaviour of electrochemically nanostructured specimens in Ringer solution is shown and discussed in comparison to those derived with polished surfaces. [1] R. Büscher et al. In W.J. Bartz (Ed.) 13th International Colloquium Tribology, Lubricants, Materials, and Lubrication Engineering (Proc. Conf.). January 15 - 17, 2002, Stuttgart / Ostfildern, Germany Technische Akademie Esslingen, Stuttgart, Germany (2002) Pp.1297-1305.

3:30 PM **I2.6**

**PLASTICITY IN NANOMATERIALS.** Amiya K. Mukherjee, University of California, Dept of Chemical Engineering & Materials Science, Davis, CA.

Nanocrystalline materials contain a very large density of grain boundaries. Therefore, they have attracted considerable discussion on the extension of grain boundary related deformation mechanisms such as Coble creep and superplasticity. Bulk nanocrystalline materials provide an opportunity to investigate the scalability of grain size dependent phenomenon to a much finer scale. The application of the constitutive relation for elevated temperature plasticity to high strain rate superplasticity and also to low temperature superplasticity has been illustrated. Experimental data demonstrates that superplasticity of nanocrystalline metals and alloys follows the general trend of the constitutive relation but with important differences in the level of stress and strain hardening rates. The nanocrystalline materials were produced using a variety of techniques. Nanocrystalline superplasticity was investigated in specimens produced by high-pressure torsion. Creep and superplasticity in silicon nitride nanocomposite were prepared by pyrolysis of liquid polymer precursor and subsequent compaction of the amorphous ceramic powder. Nanostructured thin film multilayers were produced by using electrodeposition or magnetron sputtering techniques. A two-phase nanocrystalline matrix was also produced by crystallization of a multicomponent iron-based metallic glass. Their microstructure, some preliminary mechanical properties at elevated temperatures, and possible deformation mechanisms will be presented. The ceramic nano-nano composites exhibited extremely low creep rates. The metallic nanomaterials demonstrated both high strain rate and low temperature superplasticity. They also exhibited very high flow stresses and strain hardening rates that cannot be explained by either grain growth or dislocation storage. The thin film multilayers revealed interesting scale dependent behavior at elevated temperatures. The results will be discussed in terms of creep and superplastic deformation mechanisms in the domain of significantly diminished length scales.

4:00 PM **I2.7**

**IN-SITU OBSERVATIONS OF THE DEFORMATION OF ELECTRODEPOSITED NANOCRYSTALLINE NICKEL.** K.S. Kumar, Brown University, Division of Engineering, Providence, RI; M.F. Chisholm, J.A. Horton, Oak Ridge National Laboratory, Oak Ridge, TN; and S. Suresh, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

The mechanisms of deformation of nanocrystalline metals at room temperature have been the subject of several recent computational and experimental investigations. While computational studies show a variety of deformation mechanisms to operate in these materials, their

relative dominance being influenced by grain size, little has been confirmed experimentally. Recently, we have deformed microtensile specimens of electrodeposited nanocrystalline nickel in the TEM and recorded the observations in real time using a video camera. These materials have a mean grain size in the range of 30-40 nm although an examination of the sheet cross section in the TEM confirms a columnar grain morphology with column lengths being anywhere from 3 times to 8 times the in-plane grain diameter. The in-situ observations confirm the presence of extensive dislocation activity at the crack tip in these specimens. In addition, voids form in the region ahead of the crack tip at grain boundaries and triple junctions. The formation of such voids and cracks partially relieves the constraints on the grain, permitting plastic deformation by dislocation motion and possibly twinning to progress more readily. Examination of the fracture surfaces of such specimens after the test in an SEM confirms failure by dimpled rupture. The scale of these dimples is significantly larger than the average grain size. The presence of pre-existing voids or their formation during deformation is thought to nucleate the dimples. Thus, fracture in the bulk does not propagate along grain boundaries in this material.

4:15 PM **I2.8**

**MICROSTRUCTURE AND MECHANICAL PROPERTIES OF COPPER-304 STAINLESS STEEL MULTILAYERS.** X. Zhang, A. Misra, H. Kung, J.D. Embury, and M. Nastasi, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM.

A recent topic of great interest in the area of nanomaterials is the mechanical properties of metallic multilayers with nanolayered structures. These nanolayered composite materials typically exhibit very high yield strength, which at room temperature can approach 1/2 to 1/3 of the theoretical strength. In some instances the high strength observed in these materials occurs along with the formation of metastable crystal structures. In an attempt to understand the role of metastable crystal structures on the strengthening of nanolayered composite, we have systematically studied copper and 304 stainless steel (SS) multilayer composites that were prepared by magnetron sputtering. The composites were composed of Cu and SS layers of equal thickness, with the thickness varied from 1 nm to 500 nm. The total thickness of the composite was approximately 2  $\mu\text{m}$ . Transmission electron microscopy analysis showed that the SS layer has a mixture of metastable bcc and equilibrium fcc phases. The co-existence of the two phases offers a special opportunity to study stabilization mechanisms of unusual phases at the nanometer scale. Nanoindentation measurements showed that the hardness of these nanolayered materials increases with the decreasing layer thickness, reaches a maximum value of about 5.2 GPa at the layer thickness of 20 nm, and decreases thereafter with the decrease of layer thickness. Detailed studies are in progress to understand the evolution of microstructure as a function of layer thickness and how the microstructure contributes to the strength of the composites.

4:30 PM **I2.9**

**THE EFFECT OF LENGTH SCALE OF THE DEFORMATION BEHAVIOR OF METALLIC MULTILAYERS-PART I: EXPERIMENTS.** A. Misra, J.F. Bingert, D.L. Hammon, J.P. Hirth, P.M. Anderson, R.G. Hoagland, J.D. Embury, N. Nastasi, and H. Kung.

The descriptions of the mechanisms that determine the strength and failure limit of nanoscale materials lie within new, largely unexplored, realms of behavior. This presentation and its companion with the same title will discuss the effect of length scale on the deformation behavior of a series of Cu-Nb multilayers synthesized by physical vapor deposition. The layer thickness was varied from a few micrometers to a nanometer. The nanoscale multilayers exhibit extraordinary stability upon room temperature rolling to high levels of plastic strain without losing the layer structure. The Kudjumov-Sachs texture orientation observed in the as-deposited multilayers was retained after rolling. The results are in strong contrast to multilayers with micrometer layer thickness, where bulk type of texture developed at the equivalent strain level. These results suggest that the deformation took place via a coordinated slip mechanism, in which the interface plays a critical role in the homogeneous distribution of slip. Detailed discussions on the new deformation mechanisms operating at the nanometer length scale will be presented. The modeling effort will be described in a companion presentation by P.M. Anderson.

**SESSION I3: POSTER SESSION**  
Monday Evening, December 2, 2002  
8:00 PM  
Exhibition Hall D (Hynes)

### 13.1

PROPERTIES OF HIGH-STRENGTH NANOCRYSTALLINE FeCo INTERMETALLIC MATERIAL. A. Duckham, D. Zhang, C.H. Shang, R.C. Cammarata, C.L. Chien<sup>a</sup> and T.P. Weihs, Department of Materials Science and Engineering, <sup>a</sup>Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, MD.

We have produced nanocrystalline FeCo intermetallics and have performed tensile tests on these bulk materials under a variety of conditions. At room temperature the nanocrystalline FeCo is extremely strong, with yield strengths over 2 GPa measured and appreciable ductility ( $\geq 3\%$ ). The measured strengths follow a Hall-Petch dependence on grain size. Most significantly, after raising the testing temperature from room temperature to 500°C we observed only a small drop-off in strength, up to 400°C. We also varied the strain rate of testing ( $10^{-2}\text{ s}^{-1}$  to  $10^{-5}\text{ s}^{-1}$ ) and have noticed minimal strain rate sensitivity in this range. Lastly, we have investigated the mechanical anisotropic effects of crystal texture by testing specimens with different orientations relative to the original rolling direction. Higher strengths but lower ductilities were obtained when loading transverse to the rolling direction compared to parallel. FeCo alloys are the materials of choice for the fabrication of soft magnetic components used in jet engines. Such components include magnetic bearings, thrusts disks and auxiliary power units (APUs). Since these components are located in different parts of the engine, they all operate at elevated temperatures. For instance, the thrust disks and APUs operate at 250°C and 100°C respectively. The very high yield strengths that we have measured at these temperatures for our nanocrystalline material means that these components can now rotate at higher speeds and hence the operating efficiency of the engines can be improved. These exceptionally high yield strengths combined with appreciable ductility also suggest there will be other potential uses for this material.

### 13.2

SYNTHESIS OF TITANIA COATED ALUMINA PARTICLES BY A HYBRID SOL-GEL METHOD. A. Schmidt, Goshen College, Dept of Chemistry, Goshen, IN; S.B. Majumder, P.S. Dabal, and R.S. Katiyar, Univ. of Puerto Rico, Dept of Physics, San Juan, PR; and D.C. Agrawal, Indian Institute of Technology, Materials Science Program, Kanpur, INDIA.

The properties of ceramic powders can be dramatically altered by modifying their surface with thin coating of another material. In the present, work we have successfully synthesized titania coated alumina particles by a hybrid sol-gel method. The surface morphology of the coated particles shows that either individual or group of sub-micron alumina particles are coated with nano-crystalline titania coating. The thickness of the titania coating could be varied by changing the precursor sol concentration. It was observed that amorphous titania was converted to anatase phase at 400°C and minor amount of rutile phase was detected in the coated particles heat treated at higher temperature. Micro-Raman spectroscopy analysis in conjunction with the X-ray diffraction and the Fourier transformed infra-red analysis were performed to understand the nature of these coated powders after heat treated in a temperature range of 200-800°C. Through these analyses it was confirmed that the major fraction of alumina particles were coated with titania completely. The mechanical strength of titania coating was qualitatively measured by ultrasonication of the coated powders for different times and it was found that the titania coatings were well adhered on the alumina particles.

### 13.3

WAVE INDUCED NANOSTRUCTURES. A. ten Bosch, CNRS, Laboratoire de Physique de la Matière Condensée, Nice, FRANCE; E. Dehaut, CEMEF, Ecole des Mines de Paris; and Sophia Antipolis, FRANCE.

In a first order phase transition, the emerging stable phase displaces the original phase and between the two, a contact forms which propagates as an interfacial profile, providing a practical method to produce materials in thin layers. The presence and role of wave phenomena during nucleation and growth has long been a question of interest. Molecular dynamic simulations in films and aggregates have repeatedly revealed changes in the vibration spectra near a phase transition and the existence of specific wave-like motions. A model for the initiation and propagation of the phase transition near a substrate and the existence and destabilizing role of surface and acoustic waves is presented. The theory is formulated on the basis of non-stationary solutions of a Fokker Planck equation and linear stability analysis. The resulting phenomena resemble surface spinodal decomposition with self-excitation of ordered surface structures but are independent of the usual assumption of a metastable phase boundary in the bulk.

### 13.4

HYDROGEN STABILIZATION OF {111} NANODIAMOND. Amanda Barnard, Salvy Russo, Ian Snook, Dept of Applied Physics,

RMIT University, VIC, AUSTRALIA; and Nigel Marks, Dept of Applied Physics, School of Physics, University of Sydney, NSW, AUSTRALIA.

Presented here are results of *ab initio* Density Functional Theory (DFT) structural relaxations performed on dehydrogenated and monohydrogenated nanocrystalline diamond structures of octahedral {111} and cuboctahedral morphologies, up to approximately 2nm in diameter. Our results in this size range show an inward transition of dehydrogenated nanodiamond clusters into carbon onion-like structures, with preferential exfoliation of the {111} surfaces, in agreement with experimental observations. However, we have found that this transition may be prevented by monohydrogenation of the surfaces. Bonding of atoms in the surface layers of the relaxed structures, and interlayer bonding has been investigated using Wannier functions.

### 13.5

PREDICTING THE MORPHOLOGY AND MECHANICAL PROPERTIES OF DIBLOCK/NANO-ROD COMPOSITES. Zhenyu Shou, Gavin A. Buxton, and Anna C. Balazs Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA.

We couple a morphological study of a rod-filled diblock copolymer with a micromechanical simulation to determine how the spatial distribution of the rods and the copolymer domains affects the mechanical behavior of the nanocomposite. The morphological studies are conducted through a hybrid approach that couples a self-consistent field theory (SCF) for the diblocks with a density function theory (DFT) for the rods. Through these SCF/DFT calculations, we obtain the equilibrium morphology for the self-assembled diblock/rod mixture. The output of the SCF/DFT model serves as the input to the Lattice Spring Model (LSM), which consists of a three-dimensional network of springs. In particular, the location of the different phases is mapped onto the LSM lattice and the appropriate force constants are assigned to the LSM sites. A stress is applied to the LSM lattice and we calculate the elastic response of the material. We find that the local stress and strain fields are highly dependent on the properties of the constituents and morphology of the system. By integrating the morphological and mechanical models, we can establish how choices made in the components affect the ultimate performance of the material.

### 13.6

CONTROLLED MORPHOLOGY AND CHARACTERIZATION OF NANOPARTICLES AND CONDUCTING SINGLE-CRYSTAL FILMS. Anna Godfrey, Norma Alcantar, Delphine Gourdon, and Jacob Israelachvili, University of California, Dept of Chemical Engineering and Dept of Materials Science, Santa Barbara, CA.

We have investigated the processing and characterization of nanoparticle assemblies and sub-micron single-crystal films of conducting organic and inorganic materials by using the Surface Forces Apparatus (SFA) and related techniques. We have determined the effects of pressure, shear, temperature, substrate material, and electric field on the molecular alignment, and mechanical and opto-electronic properties of such materials. Newly developed methods are applied for the tailor-fabrication of micro-structured films of CdSe nanoparticles and semi-conducting optically active organic films (which could potentially replace silicon). Our techniques also allow a quantitative characterization of "structure-function" relationships associated with the collective properties of films in the thickness range from 1 to 1000 nm (10Å to 1μm) and having large areas

### 13.7

SYNTHESIS OF NANOCLAY/EPOXY COMPOSITES WITH A THREE-ROLL MILL MACHINE. Asma Yasmin, Jandro L. Abot and Isaac M. Daniel, Center for Intelligent Processing of Composites, Northwestern University, Evanston, IL.

In recent years, the addition of nanoclay particles instead of conventional filler materials (e.g. mica, silicates etc.) to a polymer matrix has shown significant improvements in mechanical, heat and barrier properties of the composite. This type of composite is now being considered for a wide range of applications like aerospace, automotive, electronics and food industries. However, the improvement of properties of nanoclay composite is directly related to the complete exfoliation of nanoclay particles in a polymer matrix and that is still a challenge. In this study, a three-roll mill machine (Ross Bench Top Model 52M 2.5" x 5") has been used to exfoliate and disperse the nanoclay particles (Nanomer 1.28E from Nanocor, Inc., USA) in an epoxy matrix. The synthesis process has been carried out with different concentrations of clay particles and mixing times. The degree of intercalation/exfoliation and the d-spacing between platelets have been investigated using X-Ray diffraction (XRD) and Transmission Electron Microscope (TEM). The mechanical and viscoelastic behavior of nanocomposites have been investigated using

servohydraulic testing machine and Dynamic Mechanical Analyzer (DMA) respectively. It is found that the longer the mixing time, the higher the degree of intercalation. Furthermore, a higher d-spacing between clay platelets can be better achieved in this synthesis process compared to other processes like direct and solvent methods. However, the mixing process with three-roll mill produces a foamy material and the degassing process has proved to be critical for the improvement of mechanical properties of the final composite.

### **I3.8**

**THE GROWTH OF HOLLOW CARBON FIBRES USING A PURE COPPER CATALYST.** Benjamin Farmer, Derek Holmes, Luc Vandeperre, Robert Stearn and William Clegg, University of Cambridge, Ceramics Laboratory, Department of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

Catalytic decomposition of methane has been used to grow bamboo structured carbon tubes at temperatures ranging from 1233 K to 1291 K. No tube growth was observed at temperatures less than 1233 K, whilst above 1291 K pyrocarbon was the dominant product. It is shown that the average size of the copper catalyst particles was influenced by the reaction temperature, with the reciprocal of the maximum size of the copper particle decreasing linearly with temperature. This is consistent with the idea that the melting point can be depressed by surface energy effects and suggests that the copper catalyst particle is molten. Observations show that the catalyst particle flows partly into the tube and a growth mechanism for the bamboo structure is proposed based upon the energy changes of the surfaces of the partially drawn-in droplet and tube during the growth process.

### **I3.9**

**STRUCTURAL CHARACTERISTICS OF ULTRATHIN SINGLE-WALL CARBON NANOTUBES.** Changyong Xiao, Jianyi Lin, Department of Physics, National University of Singapore, SINGAPORE; Xiaowei Sun, Daohau Zhang, School of Electric and Electronic Engineering, Nanyang Technological University, Singapore, SINGAPORE; and Jikang Feng, Department of Chemistry, Jilin University, Changchun, P.R. CHINA.

We first systematically represented the diameter related stability for ultrathin single-wall carbon nanotubes in view of quantum chemistry. Comparison was made with the variation of carbon-carbon bonds and electronic properties versus the tube index. With the diameter increases, the stability usually increases but with several minimum points, which depends on its geometrical index. These minimum tends to demonstrate the most difficult to obtain single-wall carbon nanotubes with narrow distribution of diameter. Further, the calculation points out that the (2,2) single-wall carbon nanotube is the one with the smallest diameter 2.71 Å that we could obtain in experiments.

### **I3.10**

**ELECTROSPINNING POLYSTYRENE FIBERS: THE EFFECT OF MOLECULAR WEIGHT ON SURFACE TEXTURE AND MORPHOLOGY.** Cheryl L. Casper, Jean Stephens, Silke Megelski, John F. Rabolt, University of Delaware, Dept of Materials Science and Engineering, Newark, DE; and Bruce Chase, Central Research and Development, Dupont, Wilmington, DE.

Electrospinning is a technique that applies an electric field to a polymeric solution in order to produce sub-micron size fibers. The shape and texture of the fibers depend upon the electrospinning parameters used. Determining the link between electrospinning parameters, such as molecular weight, and the electrospun fiber morphology will allow for the design of polymeric fibers to meet specific application needs. The effect of molecular weight on fiber formation was studied using polystyrene dissolved in tetrahydrofuran. It was found that small fibrous tails began to form on the end of droplets when the molecular weight of the polystyrene approached 75,700 grams per mole. These fibers were approximately 0.5 microns in diameter. Longer, unattached fibers with a diameter of 6 microns were produced when the molecular weight reached 171,000 grams per mole. Fibers electrospun from this molecular weight appeared to have the expected dog-bone cross-section. The diameter of the fiber did not vary greatly when increasing the molecular weight from 171,000 to 560,000 grams per mole. However, the fibers deviated from the dog-bone cross-section at the higher molecular weight. As observed by FE-SEM, these fibers appeared to have a rippled surface compared to the dog-bone shaped cross-section mentioned previously. Additional results investigating the connection between molecular weight and viscosity in effecting the resulting electrospun fibers will also be discussed.

### **I3.11**

**PREPARATION OF NANO-SCALE NOBLE-METAL POWDER BY SELF-REGULATED REDUCTION VIA REACTIVE MICELLES AS**

**TEMPLATES.** Chien-Liang Lee, Chi-Chao Wan, National Tsing Hua Univ, Dept of Chemical Engineering, Hsinchu, TAIWAN.

A new method to synthesize noble metal nanoparticles has been developed whereby an alcohol-type surfactant, sodium alkyl sulfate, is used as the reductant, and there is no need for an external reducing agent. In this method, metal ions including Pd, Pt, Ru and Ag are reduced to zero-valence atoms by self-generated long carbon-chain alcohol inside the micellar core and then hydrophilic metal nanoparticles form. By this method, in the Pd case, by changing the carbon chain length of the surfactant, the diameter of the nanoparticles can be controlled. The longer the carbon chain length is, the shorter is the particle diameter. In the Pt case, the particle diameter can be controlled between 1 and 3 nm. In the Ru case, the time to form particles is found to be shorter than that to form Pd, Pt or Ag particles and particles diameters are always around 2 nm regardless of the surfactant used. Finally, in the Ag case, by UV-Vis spectrum, the surface plasmon resonance band at about 400 nm accompanying with particle nucleation and growth is found to be continuously intense and shift toward red.

### **I3.12**

**USING GRAPHITE NANOFIBERS AND NANOTUBES AS CATALYST SUPPORT MEDIA.** Chris Marotta, R. Terry, and K. Baker, Catalytic Materials Ltd, Holliston, MA.

The electrical conductive properties of graphite offer advantages when the material is used as a catalyst medium. Unfortunately, in its conventional form of flat sheets, graphite has a low surface area ( $\sim 0.5\text{ m}^2/\text{g}$ ) and the high fraction of exposed basal plane regions are relatively inert with respect to interaction with other materials. These drawbacks can be readily overcome if one elects to use graphite nanofibers and nanotubes for this purpose. Graphite nanofibers (GNF) and nanotubes have been grown from various metals including iron, nickel, cobalt, and copper using carbon-containing gases at different temperatures. Individual GNF are typically between 5 to 50 nm in width and 5-100  $\mu\text{m}$  in length and possess an abundance of exposed edges. The crystallinity and arrangement of the graphite basal planes (002 lattice planes) can be custom tailored by judicious choice of gas feed, catalyst, temperature, and support (or its absence). Variations in surface area ( $50-300\text{ m}^2/\text{g}$ ), porosity, and edge structure can be realized by the structural promoters and post growth treatments. We have endeavored to exploit the potential of highly tailored graphite nanofibers (GNF) and carbon nanotubes (CNT) as catalysts for the low temperature oxidation of carbon monoxide. The material possesses the ideal blend of reaction sites required to optimize the catalyst performance, namely a well-defined mixture of basal plane and edge regions.

### **I3.13**

**CHARACTERIZATION OF MECHANICAL DEFORMATION OF NANOSCALE VOLUMES.** Christopher R. Perrey, William Mook, C. Barry Carter, and William W. Gerberich, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

The mechanical properties of nanoscale volumes and their associated defect structure are key to many future applications in nanoengineered products. In this study, techniques of mechanical testing and microscopy have been applied to better understand the mechanical behavior of nanoscale volumes. Nanoindentation has been used to investigate important mechanical material parameters such as the elastic modulus and hardness for single nanoparticles. These results have been compared to atomistic simulations of deformation and plasticity as a function of size for the nanoparticles. New sample preparation methods must be developed to allow the necessary TEM characterization of the inherent and induced defect structure of these nanoparticles. Issues of chemical homogeneity, crystallinity, and defect characteristics at the nanoscale are being addressed in this study. This integration of investigative methods will lead to a greater understanding of the mechanical behavior of nanostructured materials and insights into the nature of defects in materials at the nanoscale.

### **I3.14**

**INTERACTION OF CARBON NANOTUBES WITH LIQUID POLYMER.** D. Danailov, P. Kebinski, P.M. Ajayan, MS&E Department and S. Nayak, Physics, Applied Physics and Astronomy Department, Rensselaer Polytechnic Institute, Troy, NY.

Using molecular dynamics simulations we studied the interactions with liquid polymer of captured (5,5) and (10,10) carbon nanotubes (CNTs) from about 2000 and 4000 atoms respectively. All atoms from the CNTs were initialized with primary velocity and at the penetration of the CNT in the viscous liquid polymer the velocity becomes equal to zero. At velocity of about 1000 m/s the captured (5,5) CNT becomes buckled at interaction with the liquid polymer and the same can be expected for the (10,10) CNT. The effective force

at the buckling is less than the minimal constant force for the CNT deformation without interacting with liquid, but the maximal values of the force at the interaction with the liquid polymer are bigger and this cause the buckling. The simulations can be useful for estimation of the processes at preparation of nanocomposite materials in polymer matrix.

This research was support by Phillip Morris USA.

**13.15**  
**METALLIZED OPTICAL FIBER PREPARED BY MAGNETRON SPUTTERING.** D. Deligiannis and K.-Y. Wang, Intelvac, Georgetown, ON, CANADA.

Metalized optical fiber is important for hermetical sealing of optical devices, such as lasers, photodetectors, feedthroughs and sensors [1]. Typically metalized optical fibers can be prepared in two steps. The acrylate jacket of optical fiber is stripped and the stripped fiber is metalized by electroless plating or physical vapor deposition. Normally the metalization decreases the strength of optical fibers, which the strength is lower than 1.0 kg. In this paper, we report a new method for metalizing optical fiber, that multilayer thin film Ti/Pt/Au were deposited on silica optical fiber by a ring array magnetron sputtering deposition system at low temperature. The thickness of films; Ti, Pt, Au are 20 nm, 40 nm and 250 nm respectively. Scanning Electron Microscopy shows no existence of titanium on the surface of the gold film, and gold particle size is 100 nm. Mechanical strength measurements were performed on the metalized sections of optical fiber by soldering the fiber with a scale. Pull tests show that our pull force is larger than 1.0 kg. It was also found that the adhesion is dependent on the duration of atomic oxygen pre-process before deposition. As the atomic oxygen process time increases, both adhesion and circumferential homogeneity were increased. The decreases of strength of optical fiber after metalization might be due to the bonding reaction between silica and thin film titanium. [1] M.S. Chen, USA patent 6,251,252, 2001

**13.16**  
**SYNTHESIS AND CHARACTERIZATION OF METAL-CERAMIC THIN FILM NANOCOMPOSITES WITH IMPROVED MECHANICAL PROPERTIES.** D. Kumar, N. Sudhir, S. Yarmolenko, and J. Sankar, Center for Advanced Materials and Smart Structures Department of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; J. Narayan, A. Tiwari, H. Zhou and G. Duscher, Center for Advanced Materials and Smart Structures, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC; S.J. Pennycook and A. Lupini, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Thin films composite materials consisting of metallic nanocrystals embedded in an insulator host have been synthesized using alternating-target pulsed laser deposition of Fe/Ni and Al<sub>2</sub>O<sub>3</sub>. The evaluation of structural quality of the thin film composites using high resolution transmission electron microscopy and scanning transmission electron microscopy with atomic number contrast has revealed the formation of a biphase system with thermodynamically driven segregation of Ni and alumina during pulsed laser deposition. The best hardness values of the thin film composites, measured using nanoindentation techniques, was found to 20-30% larger than pure alumina films fabricated under identical conditions. The improvement in values of hardness of Al<sub>2</sub>O<sub>3</sub> thin films by embedding metal nanocrystals is related to the evolution of a microstructure which efficiently hinders the manipulation and movement of dislocation and the growth of microcracks.

**13.17**  
**Abstract Withdrawn.**

**13.18**  
**MULTISCALE MODELING OF NONLINEAR RESPONSES IN NACRE, A MODEL BIO-NANOCOMPOSITE.** Dinesh R. Katti, Kalpana Katti, Shashindra Man Pradhan, Arundhati Bhowmik, North Dakota State University, Department of Civil Engineering, Fargo, ND; Hanson Fong, and Mehmet Sarikaya, University of Washington, Materials Science and Engineering, Seattle, WA.

A multiscale modeling approach is followed for simulating and modeling nonlinear responses in nacre, mother-of-pearl. This method incorporates experimentally-determined nanoscale properties into mesoscale 3D- finite element models. Nacre is a laminated, segmented, hybrid nanocomposite with a 'brick and-mortar' nanoarchitecture incorporating 10-20 nm-thick organic matrix surrounding 200-500 nm aragonitic CaCO<sub>3</sub> pseudo-hexagonal platelets that are staggered across layers. The mechanical properties of nacre such as strength, and toughness are several orders of magnitude better than most advanced ceramics and synthetic ceramic/polymer composites. The nacre structure is observed in many mollusk species, e.g., cephalopods, bivalves, and gastropods, and has survived millions of

years of evolution. Our 3D models of nacre incorporate details of nano- and microarchitecture as well as the true pseudohexagonal crystal symmetry of aragonitic platelets. Experimentally obtained nanomechanical nanoindentation data is incorporated into mesoscale finite element models. Simulations are conducted in linear and nonlinear regime using National Center for Supercomputing Applications (NCSA) ORIGIN 2000 supercomputer. Our simulations quantitatively evaluate the role of nanoscale details such as mineral bridges through organic layers on the elastic and yield behavior of nacre. In addition, specific role plasticity and nonlinearity of responses in individual components is quantitatively evaluated. This modeling approach is focused on developing a materials design methodology that is entirely simulation based. Our results may have significant implications in biomimetic design of layered hybrid nanocomposites for practical engineering applications as wear resistant, impact resistant, tough, and durable materials mimicking nacre.

**13.19**  
**PLASMA DEPOSITION OF ULTRATHIN POLYMER FILMS ON CARBON NANOTUBES.** Donglu Shi, Tony He, Mark Schulz, Wim van Ooij, and David Mast, Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH; Jie Lian and Lumin Wang, Department of Nuclear Engineering and Radiological Science, University of Michigan, Ann Arbor, MI.

Ultrathin films of pyrrole were deposited on the surfaces of two types of carbon nanotubes, namely C-fiber and Pyrograf III using a plasma polymerization treatment. The carbon nanotubes ranged several microns in length and 30-120 nm in diameter with a circular cross section. The estimated wall thickness of the tube is about 25-30 nm for both C-fiber and Pyrograf III carbon nanotubes. High Resolution Transmission Electron Microscopy (HRTEM) experiments showed that an extremely thin film of the pyrrole layer (2-5 nm) was uniformly deposited on the outer surfaces of the nanotubes. The nanotube of all sizes exhibited equally uniform ultrathin films indicating well-dispersed nanotubes in the fluidized bed during the plasma treatment. In particular, the inner wall of the nanotube is also coated with a uniform thin film of only 1 nm. This unique nanostructure is developed for the first time and will have profound impact in many areas including electronics, functional devices, nano-biomolecular applications, and drug delivery. The deposition mechanism of ultrathin polymer film on nanotube surfaces is discussed.

**13.20**  
**GROWTH AND APPLICATIONS OF CARBON NANOTUBES ON A TUNGSTEN SUBSTRATE.** Erik Einarsson, Jun Jiao, Portland State Univ, Dept of Physics, Portland, OR; George Coia, Portland State Univ, Dept of Chemistry, Portland, OR; Jeremy Petty and Logan Love, Portland State Univ, Dept of Physics, Portland, OR.

The purpose of this research is to investigate the use of tungsten as a substrate for growing carbon nanotubes (CNTs). There are many potential applications of nanotubes grown directly on tungsten, most notably upgrading a field-emission tungsten electron source to one using a CNT as the emitter. Results of these experiments show thin CNTs (having diameters smaller than 40nm) can be grown directly from pure tungsten by chemical vapor deposition (CVD) of acetylene (C<sub>2</sub>H<sub>2</sub>) in the presence of hydrogen. In addition, growth has been observed from nickel catalyst electrochemically deposited onto tungsten by linear-sweep (cyclic) voltammetry. CVD decomposition of C<sub>2</sub>H<sub>2</sub> in the presence of H<sub>2</sub> using electrodeposited nickel on a tungsten substrate resulted in localized, high-yield patches of coils, or "nanosprings". These coils have diameters as large as 10 μm, while the tubes themselves have diameters ranging from tens to hundreds of nanometers. The large-scale structure of the coils is helical with very low pitch, and the coils can grow to lengths exceeding 10 or 20 μm. The coil growth mechanism and effects of changes in growth parameters are discussed.

**13.21**  
**TAYLORING THE SIZE DISTRIBUTION OF Al-Cu NANOPRECIPITATES IN Al VIA He IMPLANTATION.** G. Feldmann, Dep. de Fisica, Estatística e Matemática UNIJUI, Ijui, RS, BRAZIL; P.F.P. Fichtner, Escola de Engenharia UFRGS, Porto Alegre, RS, BRAZIL; and F.C. Zawislak, Instituto de Fisica, Porto Alegre, RS, BRAZIL.

We report on the results of a systematic investigation of the effects of He bubbles on the thermal stability of Al-Cu precipitates. The He<sup>+</sup> bubbles and the Al-Cu precipitates were produced by He<sup>+</sup> and Cu<sup>+</sup> ion implantation in Aluminum foils followed by high vacuum thermal annealing at temperatures from 200 to 280°C. The implantation parameters were selected to produce a Cu- and He-rich layer at about 200 nm from the sample surface. The morphology of the precipitate and bubble systems were investigated by Transmission Electron Microscopy. The Cu and He concentration-depth profiles were determined by Rutherford Backscattering and Elastic Recoil

**Detection Analysis**, respectively. The thermal evolution of the precipitate system is significantly affected by the presence of He bubbles. At 200°C the precipitates are a factor of two larger in the Al(Cu+He) than in the Al(Cu) sample. At 280°C the situation is the opposite: the precipitates are a factor of two smaller in the sample Al(Cu+He). Both effects are dependent on the He implanted fluence. This behavior is discussed considering the effects of the bubble and the precipitate systems on the point defect field of the matrix. The present work shows that He implantation can be used as a tool to tailor the size distribution of Al-Cu nanoparticles in Al.

### 13.22

#### ARC PLASMA SYNTHESIS OF NANOSTRUCTURED Fe POWDER. Gil-Geun Lee and Sung-Duck Kim, Pukyong National University, Div of Materials Science and Engineering, Busan, KOREA.

Nanostructured Fe powders were synthesized by arc plasma process using Fe bulk as a raw material. Arc plasma process mainly consists of two steps which are powder synthesis step and powder stabilization step. Synthesized Fe powders have a cell structure with a outside layer of iron oxide and a inside part of pure Fe. This outside layer was formed during powder stabilization step, and the thickness of this layer increased with increasing oxygen content in stabilizing atmosphere and with decreasing relative surface area of the formed powder. The particle size and particle agglomeration were varied with the evaporation rate of bulk material which was concerned with the chamber pressure, chamber atmosphere and input power. The magnetic properties of the synthesized Fe powder were depended on the relative thickness of oxide layer to the particle size. The effects of process parameters of synthesis and stabilization steps on the characteristics of the nanostructured Fe powder are discussed.

### 13.23

#### SIZE REDUCTION OF CLAY PARTICLES IN NANOMETER DIMENSIONS. Gopinath Mani, Qinguo Fan, Samuel C. Ugbolue, and Isabelle M. Eiff, Dept of Textile Sciences, Univ of Massachusetts Dartmouth, North Dartmouth, MA.

This research work is about combining both ball milling and ultrasonication to produce nano-size clay particles. Particle size is a crucial parameter for polymer nanocomposites. Our work emphasizes on increasing the specific surface area of montmorillonite clay by reducing the particle size to nanometer dimensions. Cloisite-15A was used in our study. The characterization of nanoparticles was done by particle size analyzer based on laser diffraction and by morphological studies. The Particle Size Distribution (PSD), Specific Surface Area (SSA), Surface Weighted Mean (SWM) and Volume Weighted Mean (VWM) of the as-received samples are 0.5  $\mu\text{m}$  to 35  $\mu\text{m}$ , 1.22  $\text{m}^2/\text{g}$ , 4.9  $\mu\text{m}$ , and 8.451  $\mu\text{m}$  respectively. The PSD, SSA, SWM and VWM of the milled samples are 0.5  $\mu\text{m}$  to 15  $\mu\text{m}$ , 2.92  $\text{m}^2/\text{g}$ , 2.053  $\mu\text{m}$ , and 3.172  $\mu\text{m}$  respectively. Ultrasonication was done on milled samples in xylene. The particles in xylene are considered as the nuclei for the formation of cavitation bubbles. The high energy produced due to the collapse of cavitation bubbles at high temperature was responsible for breaking the particles. An investigation on amplitude, pulsation rate and time of the ultrasonication process was done with respect to particle size distribution. The optimized conditions were 90% amplitude, 8 and 4 pulsation rate and 4 hours ultrasonication. When the amplitude is increased from 80% to 90%, SSA increases from 40.38  $\text{m}^2/\text{g}$  to 45.48  $\text{m}^2/\text{g}$  in 1 hour and from 35.38  $\text{m}^2/\text{g}$  to 46.98  $\text{m}^2/\text{g}$  in 4 hours. When pulsation rate is changed from 5 sec. on and 5 sec. off to 8 sec. on and 4 sec. off, SSA increases from 35.5  $\text{m}^2/\text{g}$  to 49.5  $\text{m}^2/\text{g}$ . The treated clay particles were obtained in nanometer dimensions and the reduced particle size range is from 50 nm to 350 nm, SSA is dramatically increased to 48.2  $\text{m}^2/\text{g}$  from 1.22  $\text{m}^2/\text{g}$ , SWM and VWM are drastically decreased to 128 nm and 650 nm from 4.9  $\mu\text{m}$  and 8.451  $\mu\text{m}$  respectively.

### 13.24

#### STRUCTURAL CERAMIC NANOCOMPOSITES SYNTHESIZED THROUGH IN SITU REACTIONS. Guo-Jun Zhang, Synergy Ceramics Laboratory, Fine Ceramics Research Association, Nagoya, JAPAN; Jian-Feng Yang, Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology, Nagoya, JAPAN; Motohide Ando, Synergy Ceramics Laboratory, Fine Ceramics Research Association, Nagoya, JAPAN; and Tatsuki Ohji, Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology, Nagoya, JAPAN.

Structural ceramic nanocomposites have been receiving significant attention in recent years due to their excellent properties such as high bending strength, excellent creep behavior and wear resistance. Ceramic nanocomposites are mainly fabricated by sintering mechanically-mixed powders of the component phases. However, in this case, it is not easy to homogeneously disperse the nano-sized second phase particles into the ceramic matrixes. The existence of agglomerates may act as fracture flaws during material failure and

deteriorate material strength. In this work, we investigated several ceramic composite systems by in situ reaction process, such as SiC-BN and Al<sub>2</sub>O<sub>3</sub>-SiC, and their nanocomposites have been successfully synthesized. In the in situ reaction process, the distribution and homogeneity of the second phase particles in the matrix is not so strongly dependent on the shape and particle size of the starting powders and dispersing process like in the conventional direct mechanical mixing process. On the other hand, nanocomposites with low level contamination, clean grain boundaries and high microstructural stability at high temperatures can be obtained.

### 13.25

#### DISLOCATION EMISSION FROM NANOSIZED GRAIN BOUNDARIES: AN ATOMIC PICTURE. H. Van Swygenhoven, P.M. Derlet, and A. Hasnaoui, Paul Scherrer Inst, Villigen, SWITZERLAND.

Molecular dynamics computer simulations of fully 3D-nc metals with mean grain sizes up to 20 nm have shown that there exists a critical grain size below which there is no dislocation activity. Above this limit, partial dislocations start being emitted from the GBs. The present contribution deals with the atomic mechanism behind this emission and how this mechanism is related to the GB structure. It is shown that partial dislocations are emitted from GBs places where misfit is accommodated by GB dislocations. The nucleation process is facilitated by atomic shuffling and often absorption of free volume coming from nearby triple junctions or other nearby GB dislocations is involved, in other words, the same atomic activity which has been identified as constituting the GB sliding process. The nucleation and propagation induce changes in the resultant GBD distribution and additional structural relaxation is observed in the GB. From a temporal analysis there is an indication that nucleation and propagation are separated in time. It will be discussed how the grain size affects the emission of the partials. (PRB, 2002 in press, Phil. Mag A, in press)

### 13.26

#### TENSILE PROPERTIES OF NANOCRYSTALLINE Ni: A COMPARISON BETWEEN CLUSTER ASSEMBLED, ELECTRODEPOSITED AND SEVERE PLASTIC DEFORMED SAMPLES. F. Dalla Torre, H. Van Swygenhoven, and M. Victoria.

It is by now well known that different synthesis techniques result in different microstructures and thus it is difficult to get a deep understanding of the generic mechanical behaviour. In this contribution, the microstructure of nc-Ni samples synthesized by means of inert gas condensation, electrodeposition and high pressure torsion are compared in terms of grain size and microstrain (TEM and XRD), grain size distribution, excess free volume, impurities and thermal stability. It is shown that although the mean grain size measured by XRD of the samples is not that different, there is a significant difference in microstructure. Tensile properties and hardness are measured at room temperature and compared in terms of their microstructure (Acta Mater. 2002 in press)

### 13.27

#### PRODUCTION AND MECHANICAL PROPERTIES OF NANOCRYSTALLINE INTERMETALLICS BASED ON NiAl, TiAl-X AND TiAl<sub>3</sub>-X. A. Cabrera, O. Coreño<sup>a</sup>, V. Garibay-Febles<sup>b</sup>, J.G. Cabañas-Moreno, H.A. Calderon, Depto. Ciencia de Materiales, ESFM-IPN, Mexico D.F., MEXICO; and M. Umemoto, Dept. Prod. Systems Engineering, Toyohashi University of Technology, JAPAN. <sup>a</sup>Now at Univ. Aut. Edo. Hidalgo, Pachuca, Hgo, <sup>b</sup>Now at Inst. Mex. Petroleo, MEXICO.

Production of intermetallic materials in the systems NiAl, TiAl-X and TiAl<sub>3</sub>-X (X = Cr, Mn, Fe) has been achieved by means of mechanical milling and sintering techniques. Starting from elemental powders, mixtures were milled for different periods of time in Ar. As-milled powders had crystallites sizes between 4 and 25 nm and in some cases (Ti-Al system) the room temperature phase could be already identified. Spark plasma sintering was used since it reduces both time at high temperature and consequently grain growth. The produced materials have grain sizes in the nano and microscale depending on the material and processing variables. The sintering conditions for the TiAl<sub>3</sub> materials were 1073 K and for TiAl-X materials, 1373 K with a holding time of 900 s. Sintered materials in the TiAl-X system are constituted by the  $\gamma$  and the  $\alpha_2$  phases while the TiAl<sub>3</sub>-X alloys are formed only by the cubic L<sub>1</sub><sub>2</sub> phase. The average grain size range between 30 and 280 nm. NiAl materials were sintered at higher temperatures (1173-1773 K) resulting in considerable grain growth (400 nm to 2.5  $\mu\text{m}$ ). Compression tests have been performed to evaluate their mechanical properties as a function of temperature and grains size. In all cases yield stresses higher than 1 GPa are obtained together with a ductility that depends upon temperature and grain size. No ductility is found for the smallest grains sizes tested (30 nm, TiAl<sub>3</sub>-X). However ductility can be developed in these alloys by

inducing grain growth via annealing. In such materials, a considerably high strength is retained. Discussion on the mechanism of deformation in these materials will be given.

### 13.28

#### THE EFFECT OF SOLID SOLUTION W ADDITIONS ON THE NANOSTRUCTURE OF ELECTRODEPOSITED Ni.

Hajime Iwasaki, Himeji Inst. of Tech., Dept. of Materials Science and Engineering, Hyogo, JAPAN; Kenji Higashi, Osaka Prefecture Univ. Dept. of Metallurgy and Materials Science, Sakai, Osaka, JAPAN; and T.G. Nieh, Lawrence Livermore National Laboratory, Materials Science and Technology Division, Livermore, CA.

Electrodeposition method has been developed as an important technique in LIGA process for micro-fabrication. Electrodeposited Ni-W alloy is particularly noteworthy because it has a nanocrystalline microstructure and thus high hardness. However, the exact nanostructure of the foil, e.g. grain texture and size distribution, and the nature of grain boundaries, has not been characterized. In this paper, electrodeposited Ni-W alloys were investigated in view of relationship between tungsten content and nanostructure using high-resolution transmission electron microscopy on the cross-sectional and the foil planes. The specimen was found to contain 11.8 at% of tungsten and consists of 12 % of amorphous region and 88 % of nanocrystalline grains with an average grain size of 4.5 nm. The grain boundaries are mostly low-angle. An increase in tungsten content from 11.8 at% to 12.6 at%, which was obtained by increasing the current density from  $0.10 \text{ A/cm}^2$  to  $0.15 \text{ A/cm}^2$ , increases the volume fraction of amorphous region and the grain-boundary angle.

### 13.29

#### SHAPE-MEMORY OF CARBON NANOTUBES FILLED

THERMOPLASTIC ELASTOMERS. Hilmar Koerner, Chyi-Shan Wang, University of Dayton Research Institute, Dayton, OH; Richard A. Vaia, Max D. Alexander, Nathan A. Pearce, and Heather Bentley, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Numerous examples exist of the addition of a low-volume fraction of nanoparticles to polymers providing enhanced properties relative to the neat resin or comparable to volume fractions of traditional fillers. This presentation will discuss the thermomechanical shape memory behavior of a thermoplastic elastomer filled with various amounts of carbon nanotubes (NT). Strain induced crystallization induced from deformation of the elastomer leads to a permanent strain-set. Melting of the crystallites results in rapid recovery of original shape. The addition of 0.1-5 vol% NT enables this response to be activated by light and/or electric fields. Furthermore the NT enhances modulus and modifies crystallite morphology. The shape-memory resulting from the morphology of the elastomers was investigated using DMA, XRD and DSC.

### 13.30

SYNTHESSES OF  $\text{C}_{60}$  THIN FILMS WITH THICKNESS OF NANO-SCALE. Nobuyuki Iwata, Shinji Kuroda, Hiroki Okuyama and Hiroshi Yamamoto, Department of Electronics & Computer Science, College of Science & Technology, Nihon University, Chiba, JAPAN.

One-dimensional (1D) and/or two-dimensional (2D) ordering of organic-based molecules have attracted the attention for the future nano-scale devices with the self-assembled manner. We chose  $\text{C}_{60}$  molecules as organic material because of its novel physical and electrical properties. However, electric properties of  $\text{C}_{60}$  vary under oxygen atmosphere with light radiation. In this study the differences of the growth mechanism and electric property for  $\text{C}_{60}$  thin films on natural mica substrates were investigated with and without vacuum ultraviolet radiation while growing. Whereas, electric properties of  $\text{C}_{60}$  thin films are also attracted from the point of FET-superconductivity, recently. We grew  $\text{C}_{60}$  thin films in a UHV-MBE system with a background pressure of less than  $1 \times 10^{-8}$  Torr. The growth mode changed from 3D to 3D on 2D above  $150^\circ\text{C}$  and then 2D surfaces were obtained because of the re-evaporation above  $190^\circ\text{C}$ . Highly oriented epitaxial  $\text{C}_{60}$  thin films with hexagonal closed packed structure *hcp* grew at the substrate temperature just below  $200^\circ\text{C}$ , of which surface was 2-dimensionally flat and showed 60 and 120 degrees facets. The surface roughness  $Ra$  of the films obtained at that temperature was 0.6 nm. The step height of 0.8 nm was consistent with that of  $\text{C}_{60}(002)$  *hcp* bulk. No apparent differences were detected with and without vacuum ultraviolet radiation. The resistance of the film was too high to be measured with applying the voltage in the FET configuration. Keywords :  $\text{C}_{60}$ -thin film, mica substrate, epitaxial growth, re-evaporation,

### 13.31

THE INFLUENCE OF ANNEALING ON GRAIN SIZE, LATTICE STRAIN, TEXTURE AND HARDNESS OF NANOCRYSTALLINE PERMALLOY. Hongqi Li and Fereshteh Ebrahimi, Materials Science and Engineering Department, University of Florida, Gainesville, FL.

The thermal stability of an electrodeposited nanocrystalline (average grain size = 14nm) permalloy (Ni-20%Fe) was investigated by annealing from  $373^\circ\text{K}$  to  $773^\circ\text{K}$  for 1.5 hours. The electrolyte consisted of a nickel sulfamate solution containing either iron sulfate or iron chloride. Using a conventional rotating disc electrode setup, the nickel-iron alloys were deposited onto annealed copper substrates with a 35mm diameter. After the deposition, the copper substrate was removed chemically. The grain size, the lattice strain and the texture of the deposits as a function of the annealing temperature were measured using x-ray diffraction techniques. The strength of the alloys in as-deposited and annealed conditions was evaluated by microhardness testing. The results of this study indicated that annealing at  $373^\circ\text{K}$  did not affect the grain size of the alloys, however, their internal strain was reduced slightly. With further increasing the annealing temperature up to  $573^\circ\text{K}$ , the grain size increased gradually from a starting grain size of 14nm to 21nm. Simultaneously, the lattice strain decreased. The grain size grew rapidly after annealing above  $575^\circ\text{K}$ . Consistently, approximately 90% of the internal strain was released. As-deposited alloys exhibited (111) crystallographic texture, which upon annealing became more random. The strength of the annealed permalloy deposits followed the Hall-Petch relationship.

### 13.32

#### GROWTH OF CARBON NANOTUBES IN PERIODIC ARRAYS.

Z.P. Huang<sup>a</sup>, M. Giersig<sup>b</sup>, D.Z. Wang<sup>c</sup>, B. Campbell<sup>d</sup>, M. Sennett<sup>d</sup>, D.L. Carnahan<sup>a</sup>, K. Kempa<sup>c</sup>, J.G. Wen<sup>c</sup>, and Z.F. Ren<sup>c</sup>; <sup>a</sup>NanoLab, Inc., Brighton, MA; <sup>b</sup>Hahn-Meitner-Institute, Berlin, GERMANY; <sup>c</sup>Department of Physics, Boston College, Chestnut Hill, MA;

<sup>d</sup>Material Science Team, US Army Soldier Biological & Chemical Command, Research, Natick Soldier Center, Natick, MA.

Periodically aligned carbon nanotubes have many potential applications in electronics and optics etc. In this paper, the carbon nanotubes have been grown by plasma enhanced hot filament chemical vapor deposition on two-dimensional periodic nickel dot array. The nickel dot pattern was obtained by nanosphere lithography. A single layer of polystyrene spheres (sphere diameter 1000 nm and 500 nm respectively) was uniformly coated on silicon as mask to obtain nano nickel dots in a hexagonal array. The size of the nickel dot and the spacing between them are tunable by the size of the polystyrene spheres. Well-aligned carbon nanotubes with a site density of  $10^7$  -  $10^8$  /  $\text{cm}^2$  were successfully obtained. Optical studies on these arrays will be presented.

#### SESSION I4: FRACTURE AND MECHANICAL

##### PROPERTIES - III

Chair: Ganesh Skandan  
Tuesday Morning, December 3, 2002  
Room 312 (Hynes)

### 8:45 AM 14.1

THE RELEVANCE OF RESIDUAL STRESS DISTRIBUTIONS IN NANOSTRUCTURED MATERIALS. Thomas Tsakalakos, Igor Zakharchenko, Yuriy Gulak, Ceramics Dept, Rutgers University, Piscataway, NJ; Mark Croft, Department of Physics, Rutgers University, Piscataway, NJ; Zhong Zhong, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY; Ronald Holtz, Naval Research Laboratory, Washington, DC; Subra Suresh, T.A. Venkatesh, MIT, Cambridge, MA; and Jeffrey A. Eastman, Argonne National Laboratory, Argonne, IL.

Quantitative understanding of the internal stresses field distribution under load is fundamental in the design engineering of static/cyclic load-bearing components. The manufacture/processing or duty cycle of such components made of Nanostructured materials can lead to a residual stress distribution which can dramatically alter (for good or ill) a components load capacity, and resistance to failure. For example, compressive (tensile) surface stresses tend to retard (accelerate) the surface-initiation and growth of cracks. To compound the problem the stress distribution is extremely difficult to experimentally characterize, offers little or no external evidence of its existence, and is often recognized only *a posteriori* after failure. In order to make reliable estimates of component performance it is necessary to have an accurate knowledge of these stresses. In this paper, two powerful synchrotron x-ray scattering techniques for residual strain depth-profiling and tomography-like scatter-intensity profiling of materials are presented. The techniques utilize energy dispersive x-ray scattering, from a fixed micro-volume, with micro-scanning of the specimen being used to profile its interior. The tomography-like profiles exploit scattering-cross-section variations, and can be contrast-enhanced by separately monitoring scattering from different crystal structures. The strain profiling technique is shown to finely chronicle the internal strain variation over several mm of steel. Since surface compression, by shot peening, is a classic method to fortify

against fatigue failure, the strain profile for shot-peened, surface-toughened material is determined and discussed in terms of a simple elastic-plastic stress/strain model. The residual stress profiling of fatigue deformation processes on WC/Co and Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocoatings and Cu and Ni nanocrystalline bulk specimens showed different internal stress distributions, relaxations and internal fatigue damages suggesting different mechanisms of deformation and damage. Other residual stress distributions by surface treatment processes such as laser shot peening, low plasticity burnishing, and friction welding will be also reviewed. The correlation of the internal stresses (stress gradients) with both abrasive and sliding wear properties in Nanostructured and microsize-grain coatings will be presented. These results could explain the observed enhancement of wear resistance of nanocoatings vs. conventional. A fresh approach to the fatigue crack retardation by overload and other transient effects will be also presented. Overload effects, underload effects and fatigue crack growth resistance with increasing K are all relatable to the internal stresses arising from the dislocations in the plastic zone. Preliminary experiments have shown that the probing sensitivity of the EDXRD method is sufficient to elucidate the origin of this internal stress  $K_{int}$  by mapping the internal stress tensor in and around the plastic zone of a crack in steels and other nanocrystalline alloys. Thus, it is demonstrated that, provided an accurate knowledge of the residual stress profiles generated is available and allowance is made for stress redistribution and the multiaxial nature of residual stresses, reliable predictions of damage and performance can be made. We gratefully acknowledge the support of the Office of Naval Research under grant N000149910424. Part of this work is also supported by the Defense University Research Initiative on NanoTechnology (DURINT), which is funded by a subcontract to Rutgers University through the Massachusetts Institute of Technology by the Office of Naval Research under Grant N-00014-01-1-0808.

**Keywords:** Energy dispersive x-ray diffraction, Synchrotron radiation, Residual stress distributions, fatigue.

#### 9:00 AM I4.2

**HIGH-TENSILE DUCTILITY IN NANOSTRUCTURED MATERIALS.** Yimin Wang, Mingwei Chen, and Evan Ma, Department of Materials Science & Engineering, The Johns Hopkins University, Baltimore, MD.

In spite of extensive studies, lack of tensile ductility at room temperature has been a constant problem in nanostructured materials. The low tensile ductility observed so far may not be an intrinsic property of nanostructured materials, but rather related to pre-mature catastrophic failure caused by processed flaws. In the present study, defect free pure copper with ultrafine grains was produced by using severe plastic deformation through cold rolling at cryogenic temperatures. A coexistence of high strength and tensile ductility (~30%) was experimentally observed. Interestingly, the subsequent thermal heat treatment can further increase the tensile ductility up to 65% without losing much of the high strength. Such an extraordinary combination of high strength and ductility paved the way for widespread structural applications of nanostructured materials.

#### 9:15 AM I4.3

**NANOINDENTATION STUDY OF THE HARDNESS AND STRAIN-RATE SENSITIVITY OF NANOCRYSTALLINE Fe FORMED BY MECHANICAL ATTRITION.** D. Jang, Department of Materials Sciences and Engineering; and M. Atzmon, Department of Nuclear Engineering and Radiological Sciences & Department of Materials Sciences and Engineering, University of Michigan, Ann Arbor, MI.

Characterization of the intrinsic mechanical behavior of nanocrystalline materials has often been challenging because the sample geometry may lead to experimental artifacts. One example has been the so called "inverse Hall Petch" behavior, characterized by a negative slope of the hardness vs.  $d^{-1/2}$  at small values of the grain diameter,  $d$ . Reports of this behavior have been controversial and often attributed to sample porosity. In order to eliminate such an artifact, we have used a nanoindenter to measure sample hardness. The indentation size, in the range of 100s of nm, is significantly smaller than the particle size, thus eliminating a porosity effect on the measurements. The hardness is observed to increase down to grain diameters of 16 nm, significantly beyond previous reports based on measurements on a larger scale. We attribute this difference to possible sample porosity in previous studies. Below 16 nm, a slight decrease in hardness is observed. While these data were obtained at relatively high strain rate, we also observe a deformation behavior that is dependent on the strain rate. In order to help determine the deformation mechanisms of nanocrystalline Fe, we have measured its strain-rate sensitivity,  $m$ , at room temperature using the nanoindenter at constant load. We observe  $m$  to be very small at large grain size and to increase monotonically with decreasing grain diameter. This suggests a thermally-activated deformation mechanism operating at room temperature.

This work was funded by the U.S. National Science Foundation, Grant DMR-9902435.

#### 9:30 AM I4.4

**PLASTIC DEFORMATION OF NANOCRYSTALLINE NICKEL AND NICKEL ALLOYS.** Fereshteh Ebrahimi, Materials Science and Engineering Department, University of Florida, Gainesville, FL.

Nanocrystalline pure nickel, nickel-copper and nickel-iron alloys were fabricated using the electrodeposition technique. The electrolyte consisted of a nickel sulfamate solution and the deposition was conducted galvanostatically using a rotating disc setup. The nanocrystalline metals were deposited on a copper substrate, which was subsequently removed chemically. The thickness of the deposits was in the range of 30 to 50 micrometer. The microstructure of the deposits was evaluated using x-ray diffraction and transmission electron microscopy techniques. The stress-strain behavior of the as-deposited and annealed nanocrystalline samples was evaluated as functions of test temperature and strain rate by testing dog-bone shaped tensile specimens. The deposits with grain sizes larger than approximately 25nm were quite ductile. These deposits exhibited very high initial strain hardening rates. The results of this study indicate that the strain hardening rate depends on (i) the narrowness of the grain size distribution, (ii) the presence of internal strains, (iii) the alloying content, (iv) the test temperature, and (v) the applied strain rate. The high strain-hardening rate of nanocrystalline metals and its dependency on the microstructure and testing conditions will be discussed in terms of dislocation motion in the large grains and the consequent development of internal stresses due to the plastic inhomogeneity.

#### 9:45 AM I4.5

**CHARACTERIZATION OF NANOPARTICLE FILMS AND STRUCTURES PRODUCED BY HYPERSONIC PLASMA PARTICLE DEPOSITION.** Christopher R. Perrey, Ryan Thompson, C. Barry Carter, Univ. of Minnesota, Dept. of Chemical Engineering and Materials Science, Minneapolis, MN; Ashok Gidwani, Rajesh Mukherjee, Thierry Renault, P.H. McMurry, J.V.R. Heberlein, and S.L. Girshick, Univ. of Minnesota, Dept. of Mechanical Engineering, Minneapolis, MN.

There is great potential for the application of nanostructured devices in numerous applications. Production of nanoparticle films and structures is an important area of research for the application of nanoengineered devices. However, for these devices to become a reality, a production method that can yield high-rate synthesis of nanostructured powders is necessary. The hypersonic plasma particle deposition (HPPD) process has been shown to be capable of the production of nanoparticle films and structures. Versatile in its ability to manufacture nanoparticles of different chemistry, HPPD also has the capability of in situ powder consolidation and assembly techniques. In this study, Si, SiC, and SiN films and structures have been produced by HPPD on a variety of substrates. Using novel specimen preparation techniques, these nanoparticles have been characterized by TEM. Fundamental issues of importance have been investigated for both the nanoparticle structure and the constituent nanoparticles. These issues include nanoparticle crystallinity, defect structure, and sintering behavior, as well as the chemical homogeneity and structural characteristics of the deposition. This application of microscopy to aid process development has resulted in insights into the nanoparticle formation process, as well as the dynamics of the HPPD apparatus.

#### SESSION I5: POLYMER-BASED NANOSTRUCTURED MATERIALS

Chair: Traugott E. Fischer  
Tuesday Morning, December 3, 2002  
Room 312 (Hynes)

#### 10:30 AM I5.1

**A STRUCTURE-PROPERTY STUDY OF A NANOCOMPOSITE POLY(METHYL METHACRYLATE) BONE CEMENT.** Mary Turell, Department of Orthopaedic Surgery, Brigham & Womens Hospital, Harvard Medical School, Boston, MA; Peter R. Jemian, Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL; Jan Ilavsky, National Institute of Standards and Technology, Gaithersburg, MD; and Anuj Bellare, Department of Orthopaedic Surgery, Brigham & Womens Hospital, Harvard Medical School, Boston, MA.

Poly (methyl methacrylate) (PMMA) based bone cement has been widely used for nearly four decades for fixation of total joint replacement prostheses. These orthopaedic implants provide mobility to elderly patients with severe joint disease, such as osteoarthritis. This unique structural application for PMMA requires it to be resistant to fatigue fracture since the cement is subjected to cyclic

loading during the patient's gait cycle. In this structure-property study, a nanocomposite PMMA cement was developed by replacing the 3 volume % of micrometer size barium sulfate particles that is usually present in bone cements by the same quantity of 50 nm size particles. The hard, barium sulfate particles are essential since they radiopacify cement thereby allowing orthopaedic surgeons to monitor fatigue fracture of the implanted cement using x-ray radiographs. The dispersion of barium sulfate particles in PMMA cement was characterized using low voltage scanning electron microscopy and ultra-small angle x-ray scattering (USAXS) performed at the UNICAT beamline of the Advanced Photon Source, Argonne National Laboratory, Argonne, IL. The cements containing micro-size fillers, nano-size fillers and no fillers were subjected to uniaxial tensile and fatigue tests. The effect of barium sulfate particle size on the work-of-fracture (WOF) for the microcomposite, nanocomposite, and radiolucent (no filler) cements was compared. In addition, fatigue failure of notched dogbone shaped cement specimens was measured by subjecting the cements to cyclic loading between 0 and 15 MPa at 5 Hz. The effect of barium sulfate particle size on these macroscopic mechanical properties will be presented.

#### 10:45 AM 15.2

**APPLICATION OF SIEBIMM TO OPTIMIZE THE MECHANICAL PROPERTIES OF THIN POLYMER FILMS.** Christopher Harrison, Christopher M. Stafford, Alamgir Karim, and Eric J. Amis, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD.

We use SIEBIMM (Strain Induced Elastomer Buckling Instability for Mechanical Measurements) to study the mechanical properties of polymer coatings as a function of film thickness, film composition, filler properties and loading fraction. SIEBIMM is a recently developed high-throughput technique which measures the mechanical properties of thin polymer films. We have applied SIEBIMM to measure the Young's modulus of polystyrene films (PS, Mw - 280 kg/mol) and find that it is independent of thickness for c.a. 50 nm and above. However, we find a decrease in the modulus as the film thickness approaches the radius of gyration of the polymer chain. Additionally, we have measured the Young's modulus of PS films plasticized with diethyl phthalate for loadings of up to 50%. We find that the modulus follows a sigmoidal dependence on plasticizer concentration and is lowered from 3 GPa for no loading to 0.5 GPa at maximum loading. Furthermore, we have applied SIEBIMM to thin films of an optically clear, miscible blend of Dexco Vector 4315 and 4411 polystyrene-polysoprene triblock copolymers. We demonstrate that the blending ratio of these two triblocks can be used to tune the resulting modulus from 5 to 100 MPa and examine the relation between block copolymer morphology (e.g. microdomain correlation length and island terracing) and resulting mechanical properties. Finally, we examine the influence of nanocomposites (e.g. montmorillonite or nanotubes) on the mechanical properties polymer coatings. Special attention is given to the degree of exfoliation for clays and dispersivity for nanotubes.

#### 11:00 AM 15.3

**BIODEGRADABLE POLYESTER-LAYERED SILICATE NANOCOMPOSITES.** Pralay Mati, Emmanuel P. Giannelis, Cornell University, Material Science and Engineering, Ithaca, NY; and Carl A. Batt, Cornell University, Department of Food Science, Ithaca, NY.

Concerns over the persistence of plastics in the environment, shortage of landfill space, increased cost of solid waste disposal, emissions during incineration, and negative impact on wildlife through ingestion and entrapment have increased research and development efforts on biodegradable polymers. The challenge remains to design biodegradable alternatives to conventional plastics that combine the mechanical and physical properties of the latter, yet they are susceptible to microbial and environmental degradation without adverse effect on the environment. Improvements in biodegradability typically, however, come at the expense of performance and trade-offs often need to be made in achieving performance while maintaining biodegradation. Polymer nanocomposites made by incorporating nanometer size inorganics into a polymer matrix offer for the first time the potential to avoid these trade-offs and thus design materials with unique properties. Nanocomposites of  $\alpha$ -hydroxy polyester, poly(lactics) (PLA) and  $\beta$ -hydroxy polyester, poly(hydroxybutyrate) (PHB) with layered silicates have been successfully prepared by melt extrusion of PLA and PHB with organically modified montmorillonite (MMT) and fluoromica. Nanostructure and biodegradability of the nanocomposites will be presented and discussed.

#### 11:15 AM 15.4

**DISPERSION CHARACTERIZATION OF METAL-OXIDE NANOPARTICLES IN POLYMERIC COATINGS.** Li-piin Sung, Manna Baghai-Anaraki, Stephanie Scierka, Building Materials Division, NIST, Gaithersburg, MD; and Derek L. Ho, NIST Center for Neutron Research, Gaithersburg, MD.

Metal-oxide particles (or pigments), such as  $TiO_2$  and  $ZnO$ , serve a number of functions in many polymeric building materials. Traditionally, they have been used as pigments to enhance the appearance properties and improve durability of polymeric products, and they have been considered to be inert. Little regard has been given to understanding potentially important effects related to their photocatalytic and semiconductor properties. Recent research on  $TiO_2$  films has revealed photocatalytic activity under ultraviolet (UV) irradiation that might degrade the polymer or might be used in mineralizing chemicals and bacteria. As nanosized particles, these materials exhibit optimal UV absorption, a benefit that currently has been exploited only in sunscreen applications. Also, these nanoparticles would likely enhance the stiffness, toughness, and service life of polymeric materials, for example, in applications in which wear resistance is important. To achieve the optimal material properties of those metal-oxide nanoparticle/polymeric composites, we need to characterize the microstructure and dispersion (sizes and spatial distribution) of nanoparticles from different process conditions, and relate the key parameters, which affect the physical and mechanical properties. In this project, non-destructive characterization methods, such as small angle neutron scattering (SANS) and laser scanning confocal microscopy (LSCM), will be used to determine the size dispersion of nano-pigment (mainly  $TiO_2$  in different particle sizes under different dispersion times and pigment concentrations) in the solution and polymer binders (solvent-based and water-borne). The results will be compared to the results obtained from conventional, destructive techniques such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM). These destructive microscopic techniques usually require a great deal of sample preparations, which may result in residual artifacts.

#### 11:30 AM 15.5

**EFFECTS OF DISPERSION, ALIGNMENT AND PERCENT LOAD ON PROPERTIES OF NANOPARTICLES IN POLYCARBONATE.** Elizabeth A. Welsh, J.B. Wright, Michael Sennett, John Song, David Zeigler, U.S. Army Soldier and Biological Chemical Command, Natick Soldier Center, Materials Science Team, Natick, MA; Z.F. Ren, W.Z. Li, and J.G. Wen, Department of Physics, Boston College, Chestnut Hill, MA.

Dispersion and alignment of carbon nanoparticles in polycarbonate have been studied. A series of thermoplastic polymer nanocomposites were prepared with a variety of carbon nanoparticle reinforcements, including multiwall carbon nanotubes, exfoliated graphite nanoparticles and conventional furnace blacks. The structures were characterized using transmission electron microscopy. The effects of particle morphology on the tensile and compressive strength of nanocomposites were evaluated. The ability to control the dispersion and alignment of carbon nanoparticles in polymers is expected to lead to the development of nanocomposites with enhanced electronic and structural properties.

#### 11:45 AM 15.6

**SYNTHESIS, PROCESSING, AND PHYSICAL PROPERTIES OF SINGLE WALL CARBON NANOTUBE REINFORCED POLYMER NANOCOMPOSITES.** Cheol Park<sup>a</sup>, Kristopher E. Wise<sup>a</sup>, Zoubeida Ounaies<sup>b</sup>, Roy E. Crooks<sup>c</sup>, Dennis C. Working, Sharon E. Lowther, Peter T. Lillhei, Emilie J. Siochi, and Joycelyn S. Harrison, <sup>a</sup>ICASE, <sup>b</sup>Virginia Commonwealth University, <sup>c</sup>Lockheed Martin, Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton VA.

Single wall carbon nanotube (SWNT) reinforced polymer nanocomposites were studied in an attempt to develop multifunctional structural materials. Kinetically and thermodynamically stable solutions of SWNT and a series of polymers were prepared and processed into various forms such as films, fibers, and moldings. Uniform dispersion of thin SWNT bundles was achieved and evidenced by high resolution electron microscopy and scanning probe microscopy. Physical properties of the SWNT-polymer nanocomposites were assessed as a function of SWNT concentration. Significant reinforcing effects on mechanical, electrical, and thermal properties were noted even at low SWNT loadings. The distribution and degree of SWNT alignment were analyzed using high resolution electron microscopy and polarized Raman spectroscopy. Numerical simulations and analytical models were used to understand the experimental results.

### SESSION 15: NANOCOMPOSITES: SYNTHESIS AND PROPERTIES

Chair: Horst W. Hahn  
Tuesday Afternoon, December 3, 2002  
Room 312 (Hynes)

#### 1:30 PM 16.1

**INFLUENCE OF FILLER-FILLER AND FILLER-MATRIX**

**INTERACTIONS ON THE MECHANICAL BEHAVIOR OF POLYMER NANOCOMPOSITES.** C. Gauthier, E. Chabert, J.Y. Cavaille, L. Chazeau, GEMPPM, UMR 5510 INSA/CNRS, Villeurbanne, FRANCE; and R. Dendievel, INPG/CNRS, St. Martin d'Hères, FRANCE.

Nanocomposite materials present specific features, mainly due to their very high interfacial area, and a very short distance between reinforcing particles surface. For polymer based nanocomposites, reinforcing particles are most of the time much stiffer than the matrix. In that case, the percolation of those particles which occurs at a threshold fraction, corresponds to the formation of a network. Such a network may result from strong interactions between the surface of the dispersed particles, but softer network may appear if the particles are bound together through the interactions of their surface with polymer chains. This work reports the dynamic mechanical characterization of nanocomposites based on a poly(butyl acrylate) matrix filled with spherical particles of either polystyrene (PS,  $T_g = 100^\circ\text{C}$ ) or silica, both of diameter 120 nm. The filler content varies around the geometric percolation threshold ( $\sim 24\%$ ), from 10% to 50% vol. The relaxed modulus of these samples is found to increase with increasing filler concentration, contact area, connectivity and the strength of the filler interaction. In order to analyze and to predict the behavior of such nanocomposite materials, a modeling of the different interactions is proposed, based on a Discrete Element Approach, and allows to better understand the origin of the reinforcing effect observed.

**1:45 PM 16.2**

**INFLUENCE OF ORGANIC MODIFIERS ON THE ADHESION OF INORGANIC/ORGANIC HYBRID COATINGS.** C.J. Barbe, D.J. Cassidy, B.A. Latella, J.R. Bartlett, Materials Division, Australian Nuclear Science and Technology Organisation, Menai, AUSTRALIA.

Organic-inorganic hybrids obtained by sol-gel processing offer a versatile new approach for fabricating thin films for a wide range of applications, including sensors, waveguides, integrated optics, and corrosion and scratch resistant coatings. A critical issue for industrial applications of these coatings is their fracture behaviour and adhesion to the substrate. By controlling process variables such as the nature and volume fraction of the organic group and the heat treatment temperature, the mechanical properties of the hybrid coatings can be readily adapted for specific functions. To investigate the influence of both the connectivity of the inorganic network and the nature of the organic modifier on the final mechanical properties, a series of thin coatings were deposited on polycarbonate and stainless steel substrates by spin-coating mixtures of TEOS and selected alkyltrimethoxy silanes (MTMS, VTMS and GTMS). Simultaneous, in-situ micromechanical testing and optical microscopy was used to probe the fracture and adhesion behaviour of the coatings. The mechanical properties of the coatings were found to be strongly modulated by the size of the organic modifier. In particular, increasing the size of the organic substituent led to a corresponding increase in the ductility of the film, together with improved adhesion. The relationship between the connectivity of the inorganic network, the volume fraction and size of the organic modifier, and the mechanical response will be discussed.

**2:00 PM 16.3**

**NANOPHASE ALUMINA / POLY(L-LACTIC ACID) COMPOSITES: A NANOSTRUCTURED BIOMATERIAL FOR ORTHOPAEDIC APPLICATIONS.** Aaron J. Duglar<sup>a,c</sup>, Rena Bizio<sup>b,c</sup>, and Richard Siegel<sup>b,c</sup>; <sup>a</sup>Department of Materials Science and Engineering, <sup>b</sup>Department of Biomedical Engineering, and <sup>c</sup>Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, NY.

The objective of this study was to design scaffolds that mimic the relative composition (organic vs. inorganic) and mechanical properties of natural cancellous bone, while maintaining the enhanced cytocompatibility of nanophasic ceramics. For this purpose, three-dimensional, porous composites of nanophasic alumina in a poly(L-lactic acid) matrix were fabricated and their mechanical properties and cytocompatibility were compared to scaffolds constructed using micron-size alumina. Scaffolds composed of 100% poly(L-lactic acid) were used as controls. Field emission scanning electron microscopy was used to examine the scaffold topography with pore size and distribution determined from measurements taken on random fields of select images. Scaffold hardness, determined by Type A Durometer measurements, was similar for all scaffolds tested. Compression modulus and yield strength were increased significantly ( $p < 0.01$ ) for both the nanophasic and the micron-size composites compared to the PLLA controls. Cytocompatibility studies were performed under standard cell culture conditions using neonatal rat calvarial osteoblasts. Osteoblast proliferation, determined utilizing fluorescent DNA quantification after 3, 7, and 14 days of culture, demonstrated a significantly ( $p < 0.05$ ) higher cell density on the nanophasic composites than on either the micron-size composites or

the PLLA controls for all time-points tested. Collagen and calcium content in the extracellular matrix were determined using commercially available assays after 14 and 21 days of culture. For these reasons, three-dimensional, porous nanophasic ceramic/polymer composites are promising constructs for use in orthopaedic applications. This work was supported by Philip Morris USA and by the Nanoscale Science and Engineering Initiative of the NSF under Award Number DMR-0117792.

**2:15 PM 16.4**

**ON SYNTHESIS AND PROPERTIES OF NANOCOMPOSITES.**

Thomas Tsakalacos, James D. Idol, Richard Renfree, Richard L. Lehman, Thomas. J. Nosker, Department of Ceramics and Materials Engineering, Rutgers University, Piscataway, NJ; Ilhan A. Aksay, Daniel M. Dabbs, Department of Chemical Engineering, Princeton University, Princeton, NJ; and Kenneth E. Van Ness, Department of Physics and Engineering, Washington and Lee University, Lexington, VA.

The length scales defining structure and organization determine the fundamental characteristics of a material. Traditional polymeric composite materials exhibit organization on two length scales: the molecular scale, e.g., the unit cell of the crystal through folding chain or the local arrangement of amorphous polymer phase, and the scale particles/phases within the composite, typically much longer length and on the order of micrometers or greater. In immiscible polymer blend materials (IMPB), however, we observe melt domains in the nanoscale range with very large aspect ratios are capable of being generated by manipulating shear rate, temperature and viscosity during melt processing and by selecting the polymer pair to conform to the requisite viscosity/volume fraction relationship. Properties of IMPB's have recently shown remarkable enhancements. Nanotechnology of dispersion of nanoparticles in IMPB's has also been found to be critical component in fabricating nanocomposites of extraordinary structural and functional performance. Among the various methods that are currently used are functionalization techniques such as coating of nanoparticles with proper material in order to maximize homogeneity of dispersed nanoparticles in the polymer matrix. Moreover, inorganic structures form via template-assisted self-assembly, where self-assembled organic material (e.g., proteins and/or lipids) form the structural scaffolding for the deposition of inorganic material. In some cases, structurally organized organic surfaces catalytically or epitaxially induce growth of specifically oriented inorganic thin films. Further, nature's way of mineralization uses environmentally balanced aqueous solution chemistries at temperatures below  $100^\circ\text{C}$ . This approach provides an opportunity for the processing of inorganics with nanoscale patterns. Two examples will be used to illustrate the potential of this approach. These will include L3 Nanostructured Silicates of controlled continuously adjustable size channels structures and infiltrated with polymer blends for optical and structural applications. Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and other ceramic nanoparticle PMMA/PC nanocomposites will be discussed. Other systems will be reviewed with emphasis on mechanical, magnetic and optical properties.

**2:30 PM 16.5**

**OPTIMIZATION OF MECHANICAL PROPERTIES OF AMINE- AND ANHYDRIDE-CURED EPOXY/CLAY NANOCOMPOSITES.**

J.L. Abot, A. Yasmin and I.M. Daniel, Robert McCormick School of Engineering and Applied Science, Northwestern University, Evanston, IL.

The study of organic-inorganic nanocomposites has become relevant in recent years since these materials exhibit synergistic properties derived from the two components. Thermosetting polymers like epoxies that have high mechanical properties provide a baseline for further improvement with the addition of nanoclay particles. These nanocomposites when used as the matrix of a reinforced fiber composite can lead to higher mechanical properties, in particular the matrix dominated properties. The polymer selected for this study was diglycidyl ether of bisphenol A (DGEBA) epoxy. Two different crosslinking methods were considered: anhydride curing with methyl tetrahydro phthalic anhydride and amine curing with an aromatic amine from Vantico Group. The selected nanoclay particles were Nanomer I.28E from Nanocor and Cloisite 30B from Southern Clay Products which are both onium modified montmorillonite minerals. Different amounts of clay particles were added to the epoxy and a direct intercalation method was employed to disperse them. This method consisted of an initial mixing of the particles in the hardener followed by the addition of the epoxy resin and the accelerator. Heating, stirring, and degassing were applied during the whole process. The material was then cured and several curing cycles varying temperature and time were considered. The cured material morphology including intercalation patterns and degree of cure was monitored with X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and dynamic scanning calorimetry (DSC). Nanocomposite specimens were

prepared according to ASTM standards and tested under quasi-static tensile loading in a servo-hydraulic testing machine. The elastic modulus, ultimate strength and ultimate strain were measured. Both the storage and loss moduli and the glass transition temperature were obtained from a dynamic mechanical analyzer (DMA). All properties were improved and the effect of the curing cycle on the properties was analyzed and well documented.

**2:45 PM 16.8**

**PREPARATION AND CHARACTERIZATION OF ALUMINA BASED Ti<sub>3</sub>N<sub>4</sub> NANO COMPOSITES.** Mats Carlsson, Mats Johnsson, Mats Nygren, Department of Inorganic Chemistry, Stockholm University, Stockholm, SWEDEN; and Eric Laarz, Institute for Surface Chemistry, Stockholm, SWEDEN.

Ceramic composites containing 2, 5, and 10 vol. % of nanosized commercially available TiN particles in alumina were prepared via a water based slurry processing route followed by spark plasma sintering (SPS) at different pressures (50-90 MPa) in the temperature range 1200-1800°C. The compacts could be fully densified by use of SPS already after three minutes at 1200°C and 90 MPa. The aim of the different SPS runs was to control the alumina grain growth and thus obtain different nano structure types; inter-, intra- and inter/intra-granular. These structure types will be correlated to some mechanical properties; e.g. hardness and fracture toughness.

**3:30 PM 16.7**

**REINFORCEMENT/MATRIX INTERFACE IN OXIDE NANOCOMPOSITES FOR ENHANCED FRACTURE TOUGHNESS.** R.R. O'Keefe, R.W. Carpick, R.F. Cooper, W.J. Drugan, and D.S. Stone, Program in Mechanics and Materials, NSF Materials Research Science and Engineering Center for Nanostructured Materials, University of Wisconsin-Madison, Madison, WI.

A key element in the design of ceramic-reinforced ceramic composites for enhanced fracture toughness is to tune the interface between reinforcement and matrix, thereby allowing debonding and frictional sliding as mechanisms for energy dissipation. In principle, these toughening mechanisms can be greatly enhanced in nanophasic composite ceramics over conventional composites because of the increase in ratio of surface area to volume and because of the potential to of reinforcement phases to achieve strengths approaching the theoretical limit. In this study toughening mechanisms in  $\alpha$ Al<sub>2</sub>O<sub>3</sub>/ZnAl<sub>2</sub>O<sub>4</sub> and ZnO/ZnAl<sub>2</sub>O<sub>4</sub> nanocomposites are analyzed. The nanocomposites are synthesized from de-agglomerated and reaction sintered mixtures of nanoparticle  $\gamma$ Al<sub>2</sub>O<sub>3</sub> (30-60 nm diameter) and ZnO (25 V 70 nm, aspect ratio > 3:1). Indentation fracture toughness measurements reveal composite toughnesses of 2 V 4 MPa-m<sup>1/2</sup>, relative to monolithic ZnAl<sub>2</sub>O<sub>4</sub> and ZnO, approximately 1 MPa-m<sup>1/2</sup> each. Furthermore, from the analysis of crack morphology, toughening mechanisms can be interrogated. The ratio of the critical energy release rate of reinforcement-matrix interface relative to that of the  $\alpha$ Al<sub>2</sub>O<sub>3</sub> reinforcement is estimated at 0.7. The effects of introducing P<sup>5+</sup> and Ti<sup>4+</sup> dopants to alter the interface structure and toughness are explored.

**3:45 PM 16.8**

Abstract Withdrawn.

**4:00 PM 16.9**

**SURFACE PROPERTIES OF ION-IMPLANTED NANO-WC/Co COMPOSITES.** S.-C. Liao, S.-W. Huang, G.W. Shyu, Materials Research Lab., Industrial Technology Research Institute, Chutung, TAIWAN; T. Vilaithong and L.D. Yu, Fast-Neutron Research Facility, Chiang Mai University, Chiang Mai, THAILAND.

In this study, we investigated the surface properties of WC/10Co/0.4VC composites implanted by various species and doses of ions. There are several important results emerging from this investigation, some of which are exemplified as follows. Through nanoindentation testing, we found that ion-implantation treatment increased surface hardness up to 29 GPa, but decreased surface elastic-modulus. Grazing incidence x-ray diffraction (GIXRD) analysis of the subsurface showed first no evidence of the formation of new compounds, and secondly peak broadening that is attributed to the WC nano-grains (as small as 40 nm) and the micro-stress (up to 5 GPa). Transmission electron microscopy (TEM) of implanted surface revealed highly dense dislocation entanglements, intersections of nano-twins, and dislocation cell nanostructures in WC grains. Auger electron spectroscope (AES) analysis of the implanted sample indicated that a layer (about 120 nm thick) rich in implanted ions was formed in the subsurface. Average surface roughness measured by atomic force microscope (AFM) of the implanted samples is as low as 3.5 nm. Pin-on-disk wear tests showed that friction coefficient of implanted samples could decrease significantly to 0.17 from 0.33 of virgin materials. In addition, nanowear tests revealed that the implanted samples had much better (30% increase) wear resistance.

Scanning electron microscopy (SEM) of wear tracks on virgin and implanted samples showed that the former underwent brittle fracture wears and the latter ductile fracture wears. This study of ion-implanted nano-WC/10Co, we believe, will have a significant impact on the improvement of tool materials.

**4:15 PM 16.10**

**SYNTHESIS AND CHARACTERIZATION OF METAL NANOPARTICLES AND THE FORMATION OF METAL-POLYMER NANOCOMPOSITES.** Anshu A. Pradhan, University of Delaware, Dept. of Materials Science and Engineering, Newark, DE; S. Ismat Shah, University of Delaware, Dept. of Materials Science and Engineering, Newark, DE, Fraunhofer Center for Manufacturing and Advanced Materials, Newark, DE.

Metal nanoparticles are highly prone to oxidation due to their high surface energy and affinity for oxygen which, at times, can lead to the complete oxidation of the particles. Studying and utilizing the unique properties of metal nanoparticles requires minimizing their interaction with the atmosphere. We have used the co-condensation technique to synthesize suspensions of metal nanoparticles in isopropanol. The solvent protects the nanoparticles from the atmosphere and also helps in minimizing the agglomeration of the nanoparticles. The metal nanoparticles were characterized by Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), UV-Visible Spectrophotometry and by Thermogravimetric Analysis (TGA). The particles showed a log-normal distribution and the average particle size was below 20 nm. Polymer-metal nanocomposites were made by dispersing the metal nanoparticles in PMMA matrix by spin coating. Adherent films, fibers and free standing films could be obtained by varying the process conditions. The SEM images of the nanocomposites showed that the nanoparticles were very well dispersed over a wide area. We have also dispersed the nanoparticle into pump oil and measured the thermal conductivity of the resultant mixture. The thermal conductivity of the oil could be increased by over 40% by adding an extremely small fraction of the silver nanoparticles.

**4:30 PM 16.11**

**THERMAL AND MECHANICAL PROPERTIES OF ALUMINA/POLYMETHYLMETHACRYLATE (PMMA) NANOCOMPOSITES.** Benjamin Ash, Linda Schadler, and Richard Siegel, Dept. of Materials Science and Engineering, Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, NY.

Alumina/polymethylmethacrylate nanocomposites were synthesized by free-radical polymerization. The alumina nanoparticles used in the study were produced by a forced gas condensation method and were used as received, or coated to modify the interaction between the particles and the polymer matrix. Tensile testing, differential scanning calorimetry, and dynamic mechanical thermal analysis were used to study the mechanical and thermal behavior of the resulting composites. At an optimum weight fraction, the nanocomposites showed an average of 600% increase in their strain-to-failure and the appearance of a well-defined yield point when tested in uniaxial tension. Concurrently, above a certain weight fraction, the glass transition temperature of the nanocomposites dropped by as much as 25 °C. The abrupt changes seem to indicate a threshold at which a significant volume fraction of polymer has higher mobility that brings about the decrease in  $T_g$ . Consistent with this behavior, the  $T_g$  depression was suppressed by coating the nanoparticles to make them compatible with the matrix. We investigate the role of particle size and particle/polymer interface in altering the  $T_g$  and in changing the mode of deformation in the bulk polymer.

**4:45 PM 16.12**

**EFFECT OF NANOPARTICLE POLYMER INTERFACE AND MICROSTRUCTURAL CHARACTERISTICS ON THE MECHANICAL BEHAVIOR OF A COMPOSITE.** Rajesh Raghavan, Craig Carter, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

The mechanical behavior of a polymer composite depends on the combined characteristic relaxation times of its constituents as well as its microstructural length scales. Rigid-particle-filled polymer nanocomposites with various microstructures and material components have been analysed with an image-based finite element approach. We obtain direct results for the macroscopic deformation properties for composites with specified components and therefore can analyze the correlation between the polymer composite microstructure and the macroscopic mechanical behaviour. Virtual dynamical mechanical analysis and strain rate tests provide insight into the role of microstructure on the average mechanical properties and their variations. The characteristics of the polymer filler interface properties is shown to have a large effect on macroscopic deformation behaviour. We present results on the interplay of multiple structural relaxation time scales that are inherent in the polymer composite material and its effect on the macroscopic properties.

SESSION I7: POSTER SESSION  
Tuesday Evening, December 3, 2002  
8:00 PM  
Exhibition Hall D (Hynes)

I7.1

EFFECT OF NANO-SIZED  $Pb(Zr_{1-x}Ti_x)O_3$  POWDERS ON ENHANCING CRYSTALLIZATION KINETICS OF  $Pb(Zr_{1-x}Ti_x)O_3$  THIN FILMS PREPARED BY METAL-ORGANIC DECOMPOSITION PROCESS. Mao-Ying Teng, National Tsing-Hua Univ, Dept. of Materials Science and Engineering, Hsin-Chu, TAIWAN; I-Nan Lin, Yin-Chih Lin, National Tsing-Hua Univ, Materials Science Center, Hsin-Chu, TAIWAN; Yi-Ming Chen, Nyan-Hua Tai, National Tsing-Hua Univ, Dept. of Materials Science and Engineering, Hsin-Chu, TAIWAN; and Hsiao-Fung Cheng, National Taiwan Normal Univ, Dept of Physics, Taipei, TAIWAN.

Ferroelectric thin films can potentially be used as microsensors, microactuator and nonvolatile cells and, thereafter, have attracted intensive investigation in recent years. Among the techniques applicable for the deposition of ferroelectric thin films, metal-organic decomposition (MOD) of precursors possess overwhelmingly advantage over other techniques in the simplicity in process, precise ness in compositional control and easiness in scaling-up of process. However, the drawback of MOD technique is the necessity of high post-annealing temperature for converting the amorphous materials into perovskite phase, which usually induces PbO-vaporization loss, degrading the ferroelectric properties of the films. Therefore, the enhancement on the crystallization kinetics for MOD-derived materials is urgently needed for the purpose of improving the characteristics of ferroelectric films. In this paper, we used nano-sized PZT powder prepared by alkoxide process to modify the crystallization behavior of MOD derived-films. Incorporation of nano-sized  $Pb(Zr_{1-x}Ti_x)O_3$ , PZT, powders ( $\sim 50$  nm) were observed to enhance markedly the crystallization kinetics of the Pb-, Zr- and Ti- carboxylates, spin-coated on Pt-coated silicon substrates. X-ray diffraction and scanning electron microscopic analyses indicate that the post-annealing temperature necessary to form perovskite phase decreases from  $600^\circ C$  for pure carboxylates to  $550^\circ C$  for nano-PZT powders incorporated ones. The beneficial effect of nano-PZT powders incorporation, in addition to the enhancement on the crystallization kinetics for PZT carboxylates, is the improvement on the stability of the PZT films. The nano-PZT powder incorporated PZT films can survive higher post-annealing temperature ( $700^\circ C$ ), achieving better ferroelectric properties ( $Pr=22.2 \mu C/cm^2$  and  $Ec=38.2 KV/cm$ ).

I7.2

MODELING MECHANICAL PROPERTIES OF CARBON MOLECULAR CLUSTERS AND CARBON NANOSTRUCTURAL MATERIALS. Iou, S. Petroniuk, V.M. Levin, and I.V. Ponomareva, Lab. of Acoustic Microscopy, Inst. of Biochemical Physics, Russian Academy of Sciences, Moscow, RUSSIA.

Three basic molecular forms of carbon 3D diamond crystalline lattice, 2D graphene sheet and 1D carbone chain, give rise a variety of macromolecular clusters and carbon nanostructural solids. Solid carbons comprise a vast family of states, which are distinguished, first of all, in their mechanical properties. Variations of the properties are great - from hard substances (diamond and HPHT fullerite ceramics) to soft and fragile graphite or molecular fullerite crystals. Diversity of mechanical characteristics stems from the variability in nanostructural organization and combination of different types of covalent bonds ( $sp^2$  and  $sp^3$  bonding) with Van-der-Waals interaction between molecular clusters. The most of carbon states are formed by 2D structural units originated from plane or curved graphene sheets - original sheets (crystalline graphite, pyrolytic carbons, etc) or closed molecular clusters (fullerenes, nanofilaments, onion structures, soot particles). Interaction between these structural units is conducted by Van-der-Waals forces or diamond-like  $sp^3$  bonds. The concept of 2D elasticity of a graphene sheet together with the idea of stiffness of a single  $sp^3$  bond have been applied to theoretical evaluating elastic properties of diverse carbon states. 2D elastic moduli of a graphene sheet have been extracted from data on elastic moduli of crystalline graphite. Stiffness of the  $sp^3$  bond has been estimated from data on the elastic modulus of diamond along the  $\langle 111 \rangle$  direction. Efficiency of Van-der-Waals interaction has been taken from the elastic modulus  $C_{33}$  responsible for interlayer interaction between atomic sheets in crystalline graphite. A part of basic data (characteristics of single fullerene deformability) has been computed by the standard molecular dynamics method. Calculations and theoretical estimations have been performed for many carbon states - single molecular clusters (fullerenes and nanotubes), pristine crystalline fullerite, different HPHT phases of polymerized  $C_{60}$ , pyrolytic carbons, carbon fibers, etc. The estimations are in good agreement with experimental data on elastic properties and nanoscale structure of carbon states. The

approach is a very effective for establishing interrelation between nanostructure and elastic properties of carbon states, for prediction and classification of nanostructure in novel carbon materials on the base of data on their mechanical properties.

I7.3

MODELING SELF-ASSEMBLY OF NANOPARTICLE STRUCTURES: SIMULATION OF NANOPARTICLE CHEMICAL POTENTIALS IN POLYMER-NANOPARTICLE MIXTURES. M. Krishna Tej and J. Carson Meredith, Georgia Tech, School of Chemical Engineering, Atlanta, GA.

Nanoscale colloidal dispersions play an important role in most synthesis and processing steps for nanoscale structural materials. In many experimental approaches to dispersion and self-assembly of nanoscale colloids, surfactants in the form of oligomers or polymers are added to improve dispersability and control the onset of self-assembly. However, robust molecular models of the effects of these organic modifiers on the thermodynamic and transport properties of colloids are not generally available. Thus, the selection of appropriate surfactants is guided usually by empirical approaches or previous work. An important breakthrough in the development of predictive strategies for nanoscale structural material synthesis would be the development of molecular-models that account for the effect of surfactants on the thermodynamic and transport properties of nanoparticles. We present a novel application of the expanded ensemble Monte Carlo (EEMC) simulation method, which allows direct calculation of the chemical potential of nanoparticles in nanocolloid-polymer mixtures. The chemical potential can be used to predict dispersability, self-assembly, and the thermodynamic driving forces during nanoparticle processing. The EEMC method is applied to calculate nanoparticle chemical potential in a nanocolloid-polymer solution over a wide range of relative sizes,  $0.1 < R_g/R < 12$ , where  $R_g$  = polymer radius-of-gyration and  $R$  = particle radius. These calculations are performed for both repulsive and attractive systems. The relative surfactant-to-nanoparticle size ratio,  $R_g/R$ , is found to be an important scaling variable for the chemical potential. In particular, the chemical potential is described well by  $a(R_g/R)^b$ , where  $a$  and  $b$  depend solely on chain length. These findings add valuable insight to the design of surfactants for directing the thermodynamic driving forces in nanostructured materials processing. Simulation results also compare very favorably with a recent integral equation model [Fuchs and Schweizer, *Europhys. Lett.* **51**, 621, 2000].

I7.4

THE PROSPECT FOR NANOGRAINED STRUCTURAL STEEL. J.W. Morris Jr., University of California, Berkeley, CA.

The achievement of ultrafine grain size in commercial structural steel is an active research subject, and is the specific focus of the large "supersteel" projects that are underway in Asia. Ultrafine grain size is used for three primary purposes: to increase strength via the Hall-Petch effect, to suppress the ductile-brittle transition and to increase resistance to hydrogen embrittlement. Recent research has shown that grain sizes approaching the nanoscale can be achieved in at least three ways: by ball milling powder, as is done in many materials, by severe thermomechanical processing to generate ferrite by "strain induced dynamic transformation" (SIDT ferrite), or by cyclic use of the martensitic transformation. The first two of these methods produce crystallographically incoherent ferrite while the latter produces a coherent product in which grains that are derived from the same parent austenite have well-defined crystallographic relations to one another. Incoherent ferrite has a high Hall-Petch slope, and SIDT ferrite is now used commercially in the production of low-carbon steels with exceptional strength. But, for inherent reasons, incoherent ferrite has very little ductility at grain sizes below about 1 micron. While advanced techniques, such as "dual-phase" treatments, improve the situation somewhat, nanoginned steels of this type do not now seem promising for normal structural applications. Nanoginned coherent ferrite, on the other hand, is highly promising. Because of the crystallography of the coherent transformation, grain refining coherent ferrite has a much stronger effect on fracture than on strength. Dislocated martensitic steels can be processed to have grain sizes well below 1 micron without loss of ductility, producing alloys with exceptional combinations of strength and toughness. Still further improvements appear on the horizon as the effective grain size is refined into the nanoscale.

I7.5

CONTRASTING BONDING BEHAVIOR OF ORGANIC MOLECULES ON CARBON FULLERENE STRUCTURES. J.C. Mixteco-Sánchez, Facultad de Física, Universidad Veracruzana, Xalapa, Veracruz, MEXICO; and R.A. Guirado-López, Universidad Autónoma de San Luis Potosí, San Luis Potosí, MEXICO.

We have performed semi-empirical (MNDO) as well as *ab-initio* Hartree-Fock (HF) and density functional (DF) theory calculations at  $T = 0$  to analyze the equilibrium configurations and electronic properties of spheroidal  $C_{60}$  and cylindrical 100-atom armchair (5,5) fullerenes passivated with  $SCl_3$  and  $S(CH_2)_2CH_3$  molecules. Our structural results reveal that the lowest energy configurations of the adsorbates strongly depend on their chain length and on the structure of the underlying substrate. We have found that, in the low coverage regime, both  $SCl_3$  and  $S(CH_2)_2CH_3$  molecules prefer to organize into a molecular bundle on the surface of the  $C_{60}$ , providing thus a less protective organic coating for the carbon structure. However, with increasing coverage, a transition to a uniform distribution is obtained, which actually takes place for 5 and 7 adsorbed molecules when using  $S(CH_2)_2CH_3$  and  $SCl_3$  chains respectively. On the other hand, for the tube-like arrangement, a uniform organization of the adsorbates around the tube is always preferred for the same number of thiol molecules. The sulfur–fullerene bond is considerable strong and is at the origin of sizable deformations of the carbon structures, consisting in outward and lateral displacements of the C-atoms, as well as in the stabilization of three membered rings in the case of the  $C_{60}$  fullerene. The electronic spectrum of our passivated fullerenes reveals sizable variations in the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as a function of the number of adsorbed molecules. In fact, we have obtained a transition from the well known semiconducting character of the bare  $C_{60}$  fullerene to a conducting compound (with an energy gap of  $\sim 0.4$  eV) already for the medium thiol-covered carbon structure, opening thus the possibility to manipulate the transport properties of these compounds.

#### 17.6

#### SINTERING OF NANOSIZED $Y_3Al_5O_12$ POWDERS OBTAINED BY LIQUID-FEED FLAME SPRAY PYROLYSIS. Julien Marchal, T.R. Hinklin, and R.M. Laine, University of Michigan, Dept. of Materials Science and Engineering, Ann Arbor, MI.

Our objective is to produce transparent polycrystalline ceramics by using nanopowder sintering. Sintering studies were made using high surface area ( $90m^2/g$ )  $Y_3Al_5O_12$  powders obtained by liquid-feed flame spray pyrolysis of novel metal alkoxide and carboxylate complexes. Particle surface species were found to be precursor dependent and to greatly influence the green body compaction. The influence of various binders on compaction was also studied. These studies show that  $Y_3Al_5O_12$  powders can be sintered to full density at temperature as low as  $1400^\circ C$ , using only simple inexpensive sintering methods.

#### 17.7

#### DENSIFICATION AND SINTERING OF A MICROWAVE-PLASMA-SYNTHESIZED IRON NANOPOWDER. L.J. Kecske, R.H. Woodman, and B.R. Klotz, U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD.

Powder compacts made from microwave-plasma-synthesized iron (Fe) nanopowder (Materials Modification Inc., Fairfax, VA) were sintered under hydrogen ( $H_2$ ). Results showed that without the application of pressure, the powder could not be sintered to full density. In subsequent experiments the powder was consolidated to final densities over 80% of the theoretical full density, using a plasma pressure compaction (PPC) apparatus. To provide an explanation for the difficulty in attaining full densification, the precursor powder and compacted pellet characteristics were examined by several methods. These included residual porosity by mercury pycnometry, surface area measurement by Brunauer, Emmett, and Teller (BET) analysis, and structural change by x-ray diffraction (XRD) and scanning electron microscopy (SEM). It was observed that the nanosized primary particles were aggregated into micrometer-sized dendritic structures with the appearance of tumbleweeds. The observed limitations in the densification and associated porous microstructures of the pressureless-sintered and PPC-densified compacts were rationalized in terms of the behavior of the dendritic aggregate structures rather than that of the nanosized primary particles.

#### 17.8

#### AFM-SCRATCHING INDUCED SELECTIVE ELECTRO-CHEMICAL DEPOSITION OF PALLADIUM ONTO SEMICONDUCTOR SURFACES. Lionel Santinacci, Thierry Djenizian, Helga Hildebrand and Patrik Schmuki, Dept. of Materials Science, LKO, University of Erlangen-Nuremberg, Erlangen, GERMANY. On leave from: Swiss Federal Institute of Technology Lausanne (EPFL), Dept. of Materials Science, LTP, SWITZERLAND.

Palladium is used in a number of industrial applications and fundamental studies because of its high catalytic activity for many chemical reactions [1] and recently a great deal of interest for Pd has also emerged in the semiconductor field. Pd electrodeposition

technology is often used in electronic industry replacing gold and platinum as material for interconnection. Pd films deposited onto semiconductor surfaces can also be used for electronic devices such as Schottky diodes, sensors or solar cells [2-4].

Patterned metal deposition on semiconductor surfaces is typically carried out by photolithography combined with metal evaporation, electrodeposition or molecular beam epitaxy. To increase the resolution several techniques are being used or being investigated such as electron-beam lithography (see, e.g., Ref.[5, 6]) and focused ion beam [7, 8]. Atomic force microscopy (AFM) sensitization of an organic layer [9, 10] or direct modification of the silicon substrate by local depassivation by scanning the AFM tip under bias [11] has been investigated leading to nano-scaled structures. More recently, it has been demonstrated that using AFM-scratching method as surface pre-sensitization, it is possible to selectively deposit copper onto  $p$ -Si. [12]. The present work explores the possibilities to use this technique to achieve selective Pd electrodeposition on  $p$ -Si. The first step is to grow a thin oxide film. Then AFM-scratching is performed through the  $SiO_2$  layer and because of its insulating nature the thin oxide film acts as a mask for electrochemical deposition while the grooves are activated locations for the Pd deposition. The last step is the electrodeposition of sub-micrometer scaled Pd structures at the scratched locations. Characterizations by surface analytical techniques have demonstrated the total selectivity of the process and have indicated that the scratching parameters as well as electrochemical conditions play a crucial role in the process resolution.

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#### 17.9

#### NANOINDENTATION TECHNIQUE AT INVESTIGATING OF ALUMINA – CRC NANOPARTICLES COMPOSITES. Maksim V. Kireitseu, Ion Nemerenco, and Liudmila V. Yerakhavets, Institute of Machine Reliability, National Academy of Sciences, Minsk, BELARUS.

Nanoindentation experiments have been performed on alumina-chrome carbide nanoparticles composite coating on aluminum and corundum substrates. Films with thicknesses between 60 and 300  $\mu m$  prepared at various current intensities were indented with spherical indenters with nominal radii of 5, 10 and 25  $\mu m$ . The influence of deposition current and drying conditions were investigated using SEM. The suitability of this technique to determine morphology and the use of small spherical-tipped indenters to evaluate the mechanical properties of powder compacts was established. The revealed results are summarized as follows: (1) The structure, grain size and morphology strongly depend on deposition current although the film density does not. At low current intensity, the grain size is found to be close to the initial particle size, whereas at higher current intensity an apparent coarser grain size occurs that, however, also contains pores and internal voids. (2) it is expected that the higher over potential results in the coarser grain size and formation of pores at higher current intensity that caused the onset of electrolysis of the aqueous medium. The localized electrolysis and oxygen evolution near the anode, resulting in a localized change in pH of the aqueous suspension, produced particle agglomeration as well as bubble formation. (3) Spherical indentation technique is found to be effectively measured contact pressure and effective elastic modulus as function of penetration depth. The difference in contact pressure and elastic modulus vs. the indenter depth could be adjusted by the modulus vs. the ratio of the contact radius to the film thickness. The errors in the data could be also associated with radial cracks within the contact area. (4) The influence of deposition current indicates that higher current intensities and lower (10%) humidity resulted in higher contact pressure at constant contact strain. The influence of humidity was associated with denser films resulting from higher compressive stresses during faster drying. (5) Evidence of residual tensile stresses within the film manifested itself in the form of radial cracks from pores. The thicker films showed a greater influence of the cracks.

### **17.10**

**MULTILAYERED STRUCTURES BY SELF-ASSEMBLY.**  
M. Toprak, D.K. Kim, M. Mikhailova, and M. Muhammed, Dept. of Material Science and Engineering, Royal Institute of Technology, SWEDEN.

Nanoparticles, as building blocks, are important for the development of advanced, functional composite materials. Recent developments have shown that self-assembly of nanoparticles is a promising technique for the fabrication of complicate nanostructured materials. Self assembly of the nanoparticles into ordered structures on a substrate can be achieved through chemical treatment of the particle and/or substrate surface. Microcontact printing (mCP) is a non-photolithographic technique for generating patterned, self-assembled monolayers (SAM) on desired substrate materials. The assembled nanoparticles can have a dramatic effect on the physical properties of the composite. A mCP technique has been employed to form a SAM of bifunctional silane (APTMS) in the region of contact. The stamps for the mCP are prepared by polymerization of polydimethylsiloxane (PDMS) on a photolithographically-defined master. Silicon wafers containing a passive oxide layer or glass have been used as the substrate. Spatial arrangement of the nanoparticles can then be controlled by adjusting the concentration of the APTMS, the master pattern, surface treatment of the substrate, etc. Oxide or metallic particles have been assembled on the patterned surface after a surface treatment. The self-assembled layer was subsequently treated with bifunctional molecules and multilayers of the same material or composites have been thus obtained.

### **17.11**

**ADHESION OF HVOF SPRAYED NANOSTRUCTURED POLYMER-DIAMOND CONTAINING COMPOSITES.**  
Maksim Kireitseu, Ion Nemerenco, and A. Fedaravichus, Institute of Machine Reliability, National Academy of Sciences, Minsk, BELARUS.

Presently, poor available method for measuring the coating-substrate adherence in plasma-sprayed ceramic-metal-polymer diamond nanoparticles containing systems exists. Conventional pull-off methods must rely upon adhesives or other means of attachment that become unreliable at elevated temperatures, especially, it is hard to measure adhesion between metal and polymer adjacent layers. Nevertheless, an accurate method for determining the adherence of plasma-sprayed coatings to their substrates at elevated temperatures and loading would be useful. Many applications of such nanostructured coatings are in high-temperature environments. Calculations indicate that adherences as high as 103 MPa (15 000 psi) should be measurable. Moreover, the modified scheme appears easily adaptable to the making of adherence measurements at elevated temperatures. Unlike pull-off tests, the method is not dependent upon the thermal stability or properties of any adhesive or braze alloy. The relevant literature is reviewed. Our analysis is presented along with a schematic representation of the apparatus now under construction.

### **17.12**

**RHEOLOGICAL BEHAVIOUR AND MODEL OF METAL-POLYMER-CERAMIC NANOCOMPOSITE.** Maksim Kireitseu, Institute of Machine Reliability, National Academy of Sciences, Minsk, BELARUS.

To investigate strength and deformation of the metal-polymer-ceramic nanocomposite under indentation the rheological model has been developed. The nanocomposite is based on alumina, CrC nanoparticles, and polyamide components. The model is based on combined major rheological elements that gives accurate results conformed by experiments. Based on recent researches of mechanical properties of alumina-based ceramics, polymers and its composites the requirements to the rheological model have to be formulated to develop adequate model describing stress-strain state of the nanocomposite. We have suggested several requirements to be used in rheological model of the nanocomposite: The composite of hard alumina-aluminum can be presented as elastic-tenacious-plastic in nature of rheological model. Structural equation of the integral model of the nanocomposite shows as  $(H \mid N \mid St-V) - (H-N \mid H)$ . In general, a rheological equation depends on a level and form of stress applied. The polymer layer can be modeled as the rheological model from two elastic elements and one tenacious element. As a prototype of the model, we studied a model comprising the Maxwell's model and an elastic element. The rheological behavior of the model under-localized loading and different initial stress and deformation states have been studied. Final analysis gives better understanding of nanocomposite failure and degradation mechanics. An optimal rheological model has been revealed. The nanocomposite exhibits linear relation of stress curve, whereas unloaded composite shows retardation of deformations (elastic return) shown as downfall segment of the curve. The plotted relations of experimental data and calculated data have revealed very

close agreement of developed rheological model and real mechanical behavior of the nanocomposite. The above stated conditions are found to be used in investigations of mechanical and rheological properties of the alumina-aluminum-polymer-steel nanostructured composite systems. The rheological properties of the nanocomposite have been discussed.

### **17.13**

**PROCESSING OF SWNT/EPOXY STRUCTURAL NANOCOMPOSITES.** Margaret Roylance, Thomas Tiano, Brigit Fay, Foster-Miller Inc., Waltham, MA; and Ken McElrath, CNI, Houston, TX.

Single-wall carbon nanotubes (SWNTs), are fullerenes, hollow arrays of carbon atoms bonded in polycyclic aromatic form. A SWNT is, in essence, a single layer of graphite rolled into a seamless tube, the outer diameter of which may range from 0.7 to 3 nm. The tubes can be up to a few microns in length. The graphitic nature of this novel material form imparts exceptional properties that make SWNTs ideal candidates for the discontinuous phase of a nanofiber composite. SWNT nanocomposites should exhibit electrical and thermal conductivity, with extremely high strength to weight ratios. The table shows a comparison of the properties of a several structural composite reinforcing materials. It is clear from these data that SWNT-filled thermosets could represent a major advance in the state-of-the-art of structural composites. Material: SWNT Specific Gravity: 1.3 Tensile Strength(GPa): 300 Specific Tensile Strength: 231, 48 Modulus(GPa): 650-1000 Elongation At Break(%): 20 Area Under s/eCurve: 30. Before the benefits of these materials can be realized in structural applications, SWNT fillers must be dispersed in, and made compatible with the thermosetting resins traditionally used in these applications. Foster-Miller and its team has developed several technologies to produce SWNT nanocomposites, including: Improvement in dispersion and blending techniques that provide highly dispersed SWNTs in selected organic solvents. Development of improved nanotube surface modification techniques to stabilize the solvent based dispersions and provide a mechanism for load transfer from an organic matrix into the SWNT. Fabrication techniques for highly filled SWNT nanocomposites These techniques will be discussed, and mechanical properties of SWNT nanocomposites, including DMA and three point bend will be reported.

### **17.14**

**THE EFFECT OF ADAMANTANE UNIT ON THE CHARACTERISTICS OF POLYMERS CONTAINING THIS UNIT.**  
Masami Inoue, Hiroshi Yanazawa, ASET, Yokohama, Kanagawa, JAPAN; Takashi Ishizone and Hiroyuki Tajima, Tokyo Institute of Technology, Tokyo, JAPAN.

Electrical properties such as dielectric constants of polymers depend on both number of molecule in a unit volume and molecular polarizability. Therefore, the polymers containing a lot of free volume in molecular structure can be expected to lead to low-k materials. The polymers containing adamantane unit can be presumed to increase free volume on account of excluded volume effect. We synthesized various kinds of polymers containing adamantane unit in their side chain or main chain. The dielectric constants of these polymers were evaluated to be 1.9~2.8 and these values were comparable to those of fluorinore polymers, which have smallest dielectric constants in all polymers. Furthermore, these polymers had good thermal properties. For example, compared with poly-methylmethacrylate(PMMA), poly-adamantylmethacrylate(PAMA) containing one adamantane and poly-biadamantylmethacrylate(PBAMA) containing two adamantane in a monomer unit, the dielectric constants are 3.0, 2.8 and 1.9, and the temperatures of weight decreasing to 5% are 298, 315 and 388°C respectively. As the fraction of adamantane in polymers increases, these dielectric constants become smaller and these thermal stabilities become larger. The effect of adamantane that is bulky molecule can be recognized from these experimental results. The New Energy and Industrial Technology Development Organization supported this work.

### **17.15**

**FORMATION AND ENTRAPMENT OF NOBLE METAL CLUSTERS IN SILICA AEROGEL MONOLITHS BY GAMMA-RADIOLYSIS.** Jared F. Hund, Massimo F. Bertino, University of Missouri-Rolla, Dept of Physics, Rolla, MO; Guohui Zhang, Charklis Sotiriou-Leventis, Nicholas Leventis, University of Missouri-Rolla, Dept of Chemistry, Rolla, MO; and Akira T. Tokuhiro, University of Missouri-Rolla, Dept of Nuclear Engineering, Rolla, MO.

Noble metal clusters (Ag, Au) were formed in a silica aerogel matrix by gamma irradiation of hydrogels loaded with aqueous solutions containing  $Ag^{+}$  or  $[AuCl_4]^-$  ions. Hydrogels exposed to gamma rays assumed the color expected for colloidal suspensions of Ag (respectively Au) clusters. The hydrogels were subsequently washed and supercritically dried, without any evident change in color,

indicating that the metal clusters were not removed during drying. Typical gamma ray doses were between 2 and 3.5 kGy, and achieved complete reduction of hydrogels containing ion concentrations in the  $10^{-4}$ - $10^{-3}$  mol/l range. Reduction of solutions with higher concentrations was achieved by multiple irradiations. Importantly, in the case of Ag, autocatalytic reduction processes allow for gamma rays quantum efficiencies higher than unity. So, for instance, a total dose of 3.5 kGy has lead to a reduction of  $5.7 \cdot 10^{-2}$  M in a hydrogel with  $[\text{Ag}^+]=0.1$  M. Metal clusters in the aerogel monoliths were characterized with optical absorption, transmission electron microscopy, x-ray diffraction, scanning electron microscopy, and x-ray photoelectron spectroscopy. These techniques have shown that the clusters have a crystalline fcc structure, and diameters between about 20 and 90 nm. Au clusters consist of pure Au, while partial oxidation of Ag clusters was observed with XPS.

#### 17.18

**SYNTHESIS OF ZEOLITE Y NANOCRYSTALS FROM CLEAR SOLUTIONS.** Yunmei Shen, Michael P. Manning, Juliusz Warzywoda, and Albert Sacco Jr., Center for Advanced Microgravity Materials Processing, Chemical Engineering Department, Northeastern University, Boston, MA.

There have been several reports in the literature on the synthesis of small zeolite crystallites, for zeolites such as A, X, L, Beta, ZSM-5 and Silicalite. However, there are very few articles about the synthesis of nano-sized zeolite Y. We know of no investigations done on the effect of the Si/Al ratio in the starting solution on the Si/Al ratio in the crystals. This investigation examines the range of synthesis conditions for zeolite Y nanocrystals and investigates the effect of Si/Al ratio in the starting solution on the Si/Al ratio in the product crystals, the effect of sodium in the starting solution on the type of crystal formed, the effect of aging time and crystallization time on the product and product purity. A synthesis formulation proposed by Voltchev and Mintova was used as the starting point: 0.078 Na<sub>2</sub>O: 4.35 SiO<sub>2</sub>: 1.0 Al<sub>2</sub>O<sub>3</sub>: 2.35 (TMA)O: 248 H<sub>2</sub>O. Starting solutions, including the silicate solution and aluminum solution, were clear. The sodium content, Si/Al ratio, and TMA content were varied. The aging time and crystallization time were also varied. Scanning Electronic Microscopy (SEM) was used to observe the product morphology. SEM-Quantzaf (EDX) was used to measure the Si/Al ratio in the product crystals. X-ray Diffraction was used for identification of the crystalline phases in the product samples. Zeolite Y nanocrystals with zeolite A nanocrystals as an impurity were obtained with a size range of 20-100 nm through this synthesis. It was found that the higher the Si/Al ratio in the starting solution, the higher the Si/Al ratio in the zeolite Y nanocrystal products.

#### 17.19

**IN SITU PREPARATION OF POLYMER COATED AND FUNCTIONALIZED CERAMIC NANOPARTICLES.** Michael Schallehn, SusTech GmbH Co KG, Darmstadt, GERMANY; Horst Hahn, Institute of Material Science, Darmstadt University of Technology, GERMANY.

The functionalization and/or modification of ceramic nanoparticles offer new possibilities for the preparation of advanced nanocomposite materials with novel property combinations. Nanocrystalline ceramic particles coated with specially designed polymers have been prepared by a two step Chemical Vapor Synthesis (CVS) process using a hot wall reactor to synthesize the nanocrystalline ceramic core and a subsequent RF plasma reactor for the polymer coating or functionalization. By using continuous and pulsed plasma deposition and variation of the plasma parameters, such as RF power, period and duty-cycle, the structure of the polymer coating can be influenced. In addition, variation of plasma parameters and monomers allows the retention of functional groups, such as anhydrides, in the polymer coating. Typical particle radii are in the range of 3 to 5 nm with radii of the ceramic core in the range of 2 to 3 nm and a coating thickness in the range of 1 to 2 nm. The powders have been characterized by FT-IR, XRD, BET and HRTEM.

#### 17.20

**GRAIN BOUNDARY STRUCTURE IN NANOCRYSTALLINE MATERIALS.** Boris Demyanov and Mikhail Starostenkov, Altai State Technical Univ, Dept of General Physics, Barnaul, RUSSIA.

Nanocrystalline materials, the grain size of which is order of few (1-10 nm), have the special physical, electrical and magnetic properties. One of major factors influencing to a modification of their properties is the developed internal surface in nanocrystalline materials: interface boundaries and grain boundaries. In presented work the research of atomic structure of the grain boundaries in metals with fcc lattice was carried out using methods of computer simulation. It is revealed that on the grain boundaries there is a layer of a material with a changed crystalline structure, which thickness makes about 0.5 (a is a lattice constant). The structure of a layer has a symmetry not coincide with

a symmetry of fcc crystalline lattices interfaced grains. The given layer is possible to consider as grain boundary phase. For some special cases the structural elements of a layer are defined which allow to calculate electronic properties of grain boundary a phase and to determine their contribution to common properties of nanocrystalline materials.

#### 17.21

**YAG FIBER DERIVED FROM YAG NANOPOWDER/POLYMER PRECURSORS.** Min Kim, Jose Azurdia, Julien Marchal, and Richard M. Laine, University of Michigan, Ann Arbor, MI.

Nano-sized Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> powders were synthesized by liquid-feed flame spray pyrolysis of novel metal alkoxide and carboxylate complexes. By combining the nanopowder and the precursor, fibers can be produced by high pressure extrusion and spinning. Progress towards converting the resulting precursor fibers to dense ceramic fibers will be discussed. The precursor and processed fibers were characterized by XRD, TGA-DTA, SEM, TEM.

#### 17.22

**MOLECULAR DYNAMICS SIMULATIONS OF NANOCOMPOSITES FORMED BY INTERMETALLIC DISPERSOIDS OF Li<sub>2</sub> TYPE AND ALUMINUM MATRIX.** Min Namkung, Buzz Wincheski, NASA Langley Research Center, Hampton, VA; and Sun Mo Paik, Kangwon National University, Department of Physics, Chunchon, KOREA.

Molecular dynamics simulations were performed to characterize the lattice morphology in the region adjacent to the interfaces in composites formed by nanosized intermetallic dispersoids and aluminum matrices. The intermetallic compounds selected for the present study were Al<sub>3</sub>Nb and Ni<sub>3</sub>Al. The simulations were based on the modified embedded atom potentials found in an article by Baskes [1] that provides an explicit expression for a binary system and necessary parameter values for various elements. The results for both systems with coherent interfaces show the presence of lattice strain fields in the dispersoid and matrix due to the lattice parameter mismatches. These strain fields are seen to relax upon increasing the temperature. Incoherent interfaces were formed by rotating the lattice of the dispersoid with respect to that of the matrix. As numerically constructed nanosized crystallites are inevitably in the shape of a polyhedron, such a rotation produces interfacial areas where the atomic separation exceeds that of the interatomic forces. In this work, these gaps were filled with extra matrix atoms to maximize number of atoms interacting across the interface. The results showed the presence of noticeably disordered layers in the matrix lattice around the dispersoid in both systems. The calculated disorder parameter indicates that the effect of disorder at the incoherent interface boundary persists up to around 500 K and, beyond this, the thermally induced lattice disorder dominates. All these effects are found slightly more pronounced in Ni<sub>3</sub>Al. The lattice distortion and disorder formed in the interface region are believed to influence the lattice dynamics of nanocomposites and will be the subject of future study. [1] M.I. Baskes, Phys. Rev. B46, 2727 (1992).

#### 17.23

**MULTIPLE SOURCE FABRICATION OF ELECTROSPUN FIBER MATS.** Ming Wei, Nantiya Viriyabanthorn, Julie Chen, Joey Mead, and Changmo Sung, University of Massachusetts-Lowell, Lowell, MA.

Electrospinning processes use an electrical field to produce submicron size fibers with a polymer solution, however, the process can be time consuming to build up substantial thickness. Manufacturing methods to increase the deposition rate are necessary for commercial development of these materials. Issues include interaction between multiple jets and inefficient set-up if one simply increases the number of pipettes. This work investigated several novel methods to increase the rate of deposition of electrospun fibers. Microscopy was used to compare the structure of nonwoven mats produced by the new techniques to those produced by a single pipette.

#### 17.24

**THEORETICAL STUDIES OF THE THERMAL CONDUCTIVITY OF Si NANOWIRES.** Natalio Mingo, Liu Yang, Elret Corporation, NASA-Ames Research Center, Moffett Field, CA; Deyu Li and A. Majumdar, University of California at Berkeley, Dept. of Mechanical Engineering, Berkeley, CA.

We theoretically study the lattice thermal conductivity of Si nanowires, and compare with experimental results. We employ three different approaches: Callaway-Holland model, Green functions, and molecular dynamics. The Callaway-Holland model is based on adjustable parameters, chosen to account for different scattering mechanisms. Using a modified Callaway model, we have successfully fitted the measured thermal conductivity versus temperature of a series of nanowires, and also the silicon bulk, using a single set of parameters. Its physical implications will be discussed. Next we will

show a Green function technique that allows to study the phonon boundary scattering at the nanowires directly from atomistic considerations. This allows to overcome the traditionally parametric approach to boundary scattering. Instead, we are able to study the phonon mean free path as a function of the atomistic structure of the nanowire surface and the material coating it, without any parameters other than those defining the interatomic potentials. With this technique we study the transition from ballistic to diffusive regime in the phonon transport, in the case of Si nanowires coated by amorphous silica. Finally, we will present results of molecular dynamics simulations of Si bulk and nanowires at higher temperatures between 500K and 1000K. We use the Kubo formalism to obtain their thermal conductivity and study the effect of anharmonicity at these temperatures.

**17.23**  
**CONTROL OF THE MORPHOLOGY AND ORIENTATION OF ELECTROSPUN NANO-FIBERS.** Navin Bunyan, Julie Chen, Samira Farboodmanesh, and Kari Stevens, University of Massachusetts, Department of Mechanical Engineering, Lowell, MA.

Electrospinning is a nano-fiber manufacturing process that uses a voltage potential to initiate the spinning of a charged polymer solution. A jet of polymer solution is ejected from the conical formation at the tip of the orifice, towards the grounded target. As the solution travels through the air, electrostatic forces acting on different sections of the jet make it unstable, which leads to a complex behavior known as whipping. This whipping action elongates the fiber and decreases the diameter, enabling the formation of nano-fibers. The fibers are collected on the grounded target as a randomly oriented fiber mat. The primary objective of this research is to redesign the existing process to improve the control over the orientation of the deposited dry fiber on the target. Controlled fiber orientation can yield products such as braided, woven and patterned nano- and micro-structures, for very thin film applications, tissue scaffolds, nano wires and filters. A desired orientation of the fibers can be achieved by potentially addressing three aspects: the solution properties, the jet path control and the target design. The fibers can be directed towards the target by introducing a transverse electric field that causes an electric potential variation and/or by directing the airflow, which applies a mechanical force on the fibers. Desired fiber deposition on the target can be obtained by suitable charge concentration on the target by design modification. Adding conductive nano-particles to the solution can enhance the response of the polymer to electrostatic forces. A comparison between experimental and theoretical results for the above approaches will be presented.

**17.24**  
**BURSTING AND SPITTING COLLOIDAL DROPLETS.** Nicolas Tsapis, Danielle Sanzone, Darren Link and Dave Weitz, DEAS, Department of Physics, Harvard University, Cambridge MA.

We use the Leidenfrost effect to levitate droplets of water containing colloidal nanoparticles: the vapor film between the surface and the droplet prevents the droplet from wetting the surface. The resulting non-wetting droplets are then imaged as they dry, using a high-speed camera. As concentration of colloids increases, we observe that the shape of the droplet is able to become non-spherical. The presence of colloids also induces some pinning of the droplet on the surface. When pinning is strong enough, some droplets start spitting out smaller droplets. In other cases, the droplet shrinks without spitting until formation of a crust. If the crust is solid enough we observe some droplets bursting and then finally collapsing. This last observation is very similar to the thermal expansion step that has been observed in spray-drying experiments. This experiment is a good model for understanding recent spray-drying experiments where we formed large porous particles made of nanoparticles

**17.25**  
**CONDENSATION OF CARBON VAPOUR IN THE MICROWAVE OVEN.** Oxana V. Kharissova, Israel Nieto Lopez, Facultad de Ciencias Fisico Matematicas, UANL; Juan A. Aguilar, Ubaldo Ortiz, and Moises Hinojosa Rivera, Facultad de Ingenieria Mecanica y Electrica.

This work is devoted to microwave heating of graphite for studing the processing of carbon nanotubes by graphite vaporization. We have applied heating by microwaves (power 800W, frequency 2.45GHz) in air at 20-90 min. The oven temperature was approximately 1200 Celsius. The condensed material was collected on a quartz target. The samples were characterized and studied by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray diffraction. As a result, the samples were found to contain nanotubes, nanoparticles and fibres (1.30 - 2.80 micrometers) which appeared to be highly graphitized and structurally perfect. It was observed that multiwalled nanotubes can be produced in this way.

**17.26**  
**THE STRUCTURE AND PROPERTIES INVESTIGATION OF THE IMMISBLE POLYOLETHENE BLEND.** J.S. Petroniuk and O.V. Priadilova, Inst. of Biochemical Physics, Russian Academy of Sciences, Moscow, RUSSIA.

Mixing of the polymers allows to get material with positive properties omitting more expensive stages of the new polymers synthesis. A small addition of one polymer to another can result in changes of the supramolecular structure and properties. PE-PP mixture is immisble polymer blend. PE and PP form different types of crystalline structure. The paper is devoted to investigating the PE-PP blend structure and its properties. Measurement of crystalline content and melting temperature of blend show that the middle PE-PP composition is characterized by maximal degree of crystallinity. Infrared spectroscopy study also show that crystalline extent start to increase from 35% ratio of PP to PE and have maximum value for 35-65% containing. Then crystalline degree decrease because of small PE portions prevent to PP orientation. By method of electron-paramagnetic probe it have been observed that the middle compositions of the PE-PP blend are stable to the azonic oxidizing. We suppose for this case overmolecular structure exist. The microacoustical technique has been applied to study elastic properties and microstructural features of the blend. Acoustic microscopy allows to measure sonic velocities, bulk and shear elastic moduli and Poisson coefficient without sample destruction. Moduli dependence on PE-PP composition evidences structural reorganization. It has been shown general increasing of the elastic moduli and blend stiffness. It has been demonstrate that additivity of the PE-PP blend properties is destroyed. Phase distribution of the PE-PP blend has been visualized for different composition.

**17.27**  
**DEFORMATION-INDUCED CRYSTALLIZATION OF Al-BASED METALLIC GLASSES.** Rainer J. Hebert and John H. Perepezko, Dept. of Mats. Sci. Engr., University of Wisconsin-Madison, Madison, WI.

Devitrification reactions usually start as a result of heating but processes such as irradiation and deformation can also induce crystallization in glasses. The influence of deformation on the crystallization behavior of melt-spun Al88Y7Fe5 and Al85Ni10Ce5 ribbons has been addressed. A comparison between rolled and annealed Al88Y7Fe5 material from the same ribbon and subsequent TEM analysis revealed the effect of rolling on the crystallization behavior in terms of the particle density and size distribution. Crystallization occurred during the rolling of the ribbons but the particle density increased further upon annealing of the rolled sample. The as-spun ribbon, in contrast, did not crystallize under the same annealing conditions. The rolling process appears to be less influential for the crystallization behavior of Al85Ni10Ce5 ribbons. For example, isothermal DSC measurements showed no change in the transient time for nucleation with rolling. Considerably higher stress levels than for Al88Y7Fe5 ribbons were necessary to observe crystallites in Al85Ni10Ce5 based on X-ray diffraction. In order to evaluate the applicability of classical nucleation theory for rolling-induced crystallization reactions the Kashchiev equation was used to model the particle-size distribution of the rolled Al88Y7Fe5 ribbon. Additional insight was gained from the application of Ham's growth model to the primary crystallization peak in the isothermal DSC curve of the rolled Al88Y7Fe5 ribbon. These results demonstrate that deformation-annealing treatments can be an effective alternative route for microstructure control of metallic glasses. The support of the ARO (DAAD19-01-1-0486) is gratefully acknowledged.

**17.28**  
**Abstract Withdrawn.**

**17.29**  
**Abstract Withdrawn.**

**17.30**  
**NANOINDENTATION OF ULTRATHIN FILMS OF SILICATE NANOPARTICLES AND POLYELECTROLYTES: DEPOSITION PARAMETERS AND MECHANICAL PROPERTIES.** Rigoberto Advincula, Xiaowu Fan, Mi-kyoung Park, and Bob Brookins, University of Houston, Department of Chemistry, Houston, TX, and Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL.

Recently, we have investigated the layer-by-layer (LbL) electrostatic deposition of polycation and silicate (clay) nanoparticle ultrathin films. We have investigated the properties of these films using techniques such as ellipsometry, X-ray diffraction, surface plasmon spectroscopy (SPS), and atomic force microscopy (AFM), and quartz crystal microbalance, and X-ray Photoelectron Spectroscopy (XPS). In this talk, we would like to report our results on the formation of

nanstructured hybrid ultrathin films focusing on their unique mechanical properties as probed by nanoindentation experiments. Structural information such as film thickness, platelet coverage, surface morphology, roughness, etc., are important parameters for their potential use as coatings. We have investigated the relationship of several of these parameters with their mechanical hardness and modulus properties as a function of indenter probe depth in nanoindentation experiments. The ultrathin films have remarkable mechanical properties very different from polymer ultrathin films. Practical applications of these films are important for the preparation of thin film coatings and membrane devices using the (LbL) technique.

#### 17.31

**CONSTRUCTION OF NANO-STEPPED GLASS SURFACES BY USING VISCOS FLOW OF OXIDE GLASS FILMS DEPOSITED ON ULTRASMOOTH SAPPHIRE SUBSTRATES.** S. Akiba, S. Sato, A. Matsuda, T. Yamamoto, and M. Yoshimoto, Tokyo Inst of Tech, Materials and Structures Laboratory, Yokohama, JAPAN.

Although glass materials structure-controlled at the nano-scale have possibility to develop new functionalities, very few attempts have been made to investigate nano-scale behavior of glass at high temperatures. Softening behavior and viscous flow resulting from the supercooling state, which is characteristics to glass materials, are expected to be utilized for construction of novel nano-structures as well as for soldering the nano-structures. Here we report the fabrication of the nano-structure composed of oxide glass using softening and viscous flow at high temperatures. The ultra-thin films (about 5nm thick) of soda lime silica-based oxide glass were prepared by pulsed laser deposition (PLD) method on the ultrasmooth sapphire substrates with atomic steps of 0.2 nm in height and ultrasmooth terraces of 50-100 nm in width. These sapphire substrates were obtained by annealing in air at 1000°C. A soda lime silicate glass was used for the ablation target in PLD process. The specimens were annealed at several temperatures. It was observed with AFM that the surface morphologies were changed on an atomic scale by viscous flow of annealed ultra-thin film glass. From this observation, we found that the surface flattening of ultra-thin film glass became remarkable just over the glass transition temperature (about 550°C). Furthermore, the surface morphology of annealed glass film reflected the nano-stepped structure of the sapphire substrate. The nano-stepped surface was verified to be amorphous state (glass) from the halo pattern of reflection high energy electron diffraction (RHEED). It was also turned out that the surface flattening caused by viscous flow of ultra-thin film glass was dependent on film thickness. Further studies of viscous flow of ultra-thin oxide glass films may provide novel type functional nano-structures and nano-tools such as nano-adhesive for MEMS or a nano-scale insulator for biological devices.

### SESSION 18: MODELING, SIMULATIONS, AND INTERFACES

Chairs: Chandra Shekhar Pande and Subra Suresh  
Wednesday Morning, December 4, 2002  
Room 312 (Hynes)

#### 8:30 AM 18.1

**ATOMISTICALLY INFORMED CONTINUUM MODEL OF POLYMER-BASED NANOCOMPOSITES.** Catalin Picu, Alireza Sarvestani, and Murat Oztusul, Rensselaer Polytechnic Institute, Dept of Mechanical Engineering, Troy, NY.

In this work we focus on a model polymeric material filled with spherical nanoparticles. Monte Carlo simulations are performed to determine the polymer chain conformations in the vicinity of the curved interface with the filler. The structure of the interface is determined as a function of filler size (curvature) and chain length. Models of increasing complexity are considered: an athermal system with excluded volume interactions, a system in which entropic and energetic interactions take place between polymers, and a system in which both filler-polymer and polymer-polymer energetic interactions are accounted for. The total density, chain end density, chain segment preferential orientation and chain size and shape variation with the distance from the filler are determined. Continuum models are derived for the structures determined by atomistic simulations. The system in which polymers are well connected to the filler (strong filler-polymer interactions) is represented by a continuum composed of three phases: filler, bulk polymer matrix, and an interfacial layer with graded material properties. The system with weak interfaces (no filler-polymer interaction) is represented by a continuum model composed of two phases, filler and matrix, with a weak two-dimensional interface separating them. The parameters entering the continuum models are calibrated based on atomistic results. The continuum models are then used to homogenize the composite on larger scales. This procedure allows considering random filler distribution and clustering while accounting for atomistic detail.

#### 8:45 AM 18.2

**COMPUTER SIMULATION OF DISLOCATION PROPAGATION AND INTERACTION IN NANOSTRUCTURED METALLIC MULTILAYERS.** Peter M. Anderson and Qizhen Li, Ohio State University, Dept. of Materials Science and Engineering, Columbus, OH.

A cellular automaton approach is used to model the propagation and interaction of dislocations in metallic multilayers with an fcc structure. The {111} slip planes in each phase are discretized into small regular triangles, whose sides are along  $\langle 110 \rangle$  directions. The propagation of a dislocation occurs by incrementally adding slipped triangle onto the existing slipped area. The propagation path of dislocations is to lower the system energy by the greatest magnitude. The CA model also incorporates the stress contributions due to lattice mismatch, misfit dislocation substructure, and applied stress on the multilayer. As a check, the model reproduces the analytic result for the critical stress to operate a Frank-Read source in a homogeneous medium. Then, the model is employed to study how threading and interfacial dislocations respond in multilayers, for various combinations of layer thickness, lattice mismatch, misfit structure and applied stress. The talk will distinguish between confined modes in which the multilayer is able to confine deformation to individual layers vs. codeformation modes in which the dislocation slips through all layers.

#### 9:00 AM 18.3

**CONTINUUM MECHANICS-DISCRETE DEFECT MODELING AND BUBBLE RAFT SIMULATION OF CRACKED SPECIMEN RESPONSE IN NANOSCALE GEOMETRIES.** M.J. Starr, W.J. Drugan, Univ of Wisconsin-Madison, Dept of Engineering Physics, Mechanics and Materials Program, Madison, WI; D.S. Stone, Univ of Wisconsin-Madison, Materials Science and Engineering, Mechanics and Materials Program, Madison, WI; and M. Lopez-Garcia, Univ of Puerto Rico-Mayaguez, Dept of Chemical Engineering, Mayaguez, PR.

A continuum mechanics-based model is used to explore the fracture properties of nanoscale multilayered materials. Length scale appears via inclusion of potential emission of discrete dislocations from a crack tip following the Rice-Thompson approach. For nanoscale multilayers, the high density of interfaces has a strong effect on the propensity for a crack to either emit blunting dislocations, which relieve high local stresses, or not emit them, which promotes cleavage. The continued ability of cracks in a nanoscale multilayer to emit blunting dislocations is an important feature for increasing or maintaining fracture toughness. The ultimate goal is to use the model to predict how material combinations, layer thickness, crystal structure, and flaw size influence the effective fracture toughness of the material system. To confirm validity of the continuum model at the nanoscale and test certain critical predictions, viz. the directions of dislocation emission from crack tips, Bragg bubble raft experiments are performed. Perfect (dislocation-free) two-dimensional bubble rafts with sharp internal, sub-interface, and interfacial cracks are subjected to uniform displacement or traction to examine the nucleation and emission of dislocations. The application of uniform displacements and tractions on the bubble raft boundaries serve as the limiting cases of an infinitely rigid and perfectly compliant bounding layers, respectively. Bubble rafts with hexagonal and square (2-atom basis) crystal structures are employed. The continuum-based model predicts that the preferred direction of dislocation emission from the crack tip depends on how close the crack is to an interface. The experiments verify, qualitatively and quantitatively, the trends predicted by the model. Theory and experiment demonstrate transitions in emission behavior that take place over a large range of crack dimensions, crack locations, and loading conditions. Remarkably, the continuum model is confirmed to predict the crack dislocation emission behavior down to length scales approaching several atomic (bubble) spacings.

#### 9:15 AM 18.4

**COOPERATIVE PROCESSES DURING PLASTIC DEFORMATION: A MOLECULAR DYNAMICS SIMULATION.** A. Haasen, H. Van Swygenhoven, and P.M. Derlet, Paul Scherrer Inst, Villigen, SWITZERLAND.

Large-scale molecular dynamics simulations are performed to study the deformation behaviour at 800K of fully 3D nc-fcc Ni. A large sample containing 125 grains with a mean grain size of 5nm was chosen to minimize the effect of imposed periodicity used to simulate bulk properties. During uniaxial tensile deformation collective grain motion occurred and shear planes that extend over a number of grains are formed. The observed underlying mechanisms for their formation falls into three classes: (1) pure GB sliding induced migration of GBs to form a single shear interface consisting of a number of co-linear GBs, (2) coalescence of neighboring grains that have low angle GB facilitated by the propagation of the partials and subsequent reorientation of both grains (3) continuity of the shear plane by intragranular slip. Thus, as has been experimentally observed at high

strain rates in nc-Ni, collective grain processes forming shear planes are possible even at deformation levels that are significantly less than those associated with superplasticity.

**9:30 AM I8.5**

**DEFORMATION MECHANISM FOR THE CROSSOVER IN HALL-PETCH BEHAVIOR IN NANOCRYSTALLINE MATERIALS BY MOLECULAR-DYNAMICS SIMULATION.** Vesselin Yamakov, Dieter Wolf, Simon R. Phillpot, Materials Science Division, Argonne National Laboratory, Argonne, IL; Amiya K. Mukherjee, Department of Chemical Engineering and Materials Science, University of California, Davis, CA; and Herbert Gleiter, Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, GERMANY.

The mechanical behavior of nanocrystalline materials (i.e., polycrystals with a grain size of less than 100 nm) remains controversial, the observations ranging from greatly enhanced ductility to dramatically increased strength and hardness. While it is commonly accepted that their intrinsic deformation behavior arises from the interplay between dislocation and grain-boundary processes, little is known on the specific deformation mechanisms. Here we use molecular-dynamics simulations of fully 3d microstructures (of grain diameters from 7 to 32 nm) to reveal a transition from dislocation-mediated to grain-boundary mediated deformation in nanocrystalline fcc metals with decreasing grain size. This transition takes place when the dislocation stacking-fault splitting distance, determined by the stacking-fault energy and the threshold stress for nucleation of a dislocation from the grain boundary, is equal to the grain diameter. At this crossover grain size, the strain rate is found to be a minimum. This transition in the deformation mechanism provides an explanation for the crossover in the Hall-Petch behavior from hardening to softening with decreasing grain size.

**9:45 AM I8.6**

**THE EFFECT OF LENGTH SCALE ON THE DEFORMATION BEHAVIOR OF METALLIC MULTILAYERS-PART II: MODELING.** Peter M. Anderson, Ohio State University, Dept of Materials Science and Engineering, Columbus, OH; A. Misra, and J.P. Hirth, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM.

The experimental observations described in a companion presentation of the same title by Misra et al. highlight that unique, non-bulk rolling textures are achieved in nanoscale multilayered thin films. Specifically, Cu/Nb multilayers deposited with an initial Kudjumov-Sachs orientation relation between Cu and Nb grains and with an initial individual layer thickness of 75nm preserve that relation during rolling. In contrast, samples with micron-scale individual layer thickness do not. To help understand this layer-dependent response, a crystal plasticity model is presented in which the Cu and Nb phases respond by slip on  $\{111\}/<110>$  systems in the fcc Cu case, and  $\{110\}/<111>$  systems in the bcc Nb phase. Grains within each layered phase are required to plastically deform by a reduction in thickness and corresponding elongation in the rolling direction, with zero plastic strain along the transverse axis. The model also adopts the observation for nano-scale multilayers that the Kudjumov-Sachs orientation relation is preserved; in particular, the  $<111>$  Cu and  $<110>$  Nb directions remain parallel to the interface normal during rolling. The crystal plasticity model then furnishes the minimum plastic work to deform a grain, as a function of grain orientation. For Cu grains, the plastic work is invariant of grain orientation, provided the critical resolved shear stress is uniform on all fcc slip systems. However, the corresponding plastic work in Nb grains is very dependent on grain orientation and has a strong minimum. This large anisotropy serves as a driving force for Nb grains to rotate around their  $<110>$  interface normal, toward the minimum. The resulting prediction for rolling texture in Nb layers agrees well with experimental observations in nanoscale Cu/Nb multilayers.

**10:30 AM I8.7**

**EFFECTS OF TRIPLE JUNCTIONS ON DEFORMATION BEHAVIOR OF NANOMATERIALS.** Ilya Ovid'ko, Inst of Problems of Mechanical Engineering RAS, St. Petersburg, RUSSIA.

This presentation gives an overview of theoretical models describing the effects of triple junctions of grain boundaries on deformation processes in nanocrystalline materials. The special attention is paid to triple junction diffusional creep and its competition with grain boundary sliding controlled by triple junctions. Also, the role of triple junctions in crossover from grain boundary sliding to the rotational deformation mode in nanocrystalline materials is considered.

**10:45 AM I8.8**

**GRAIN BOUNDARY DISSOCIATION IN NANOCRYSTALLINE GOLD.** D.L. Medlin, D. Cohen, and G. Lucadamo, Thin Film and Interface Science Dept., Sandia National Labs, Livermore, CA; S.M.

Foiles, Materials and Process Modeling Dept., Sandia National Labs, Albuquerque, NM.

A common structural relaxation at grain boundaries in low stacking-fault-energy metals is the spreading, or dissociation, of the interface by the emission of partial dislocations. This phenomenon is of particular importance in nanocrystalline materials because it increases the volume fraction of material associated with interfacial sites and because the constraints of geometric compatibility in such small-grained systems can locally promote the dissociation. Here, through HRTEM observations and atomistic simulations, we consider the structure of dissociated boundaries in nanocrystalline,  $[110]$ -textured Au films. Our analyses of the interfacial dislocation structures in these boundaries show how the stacking arrangement within the dissociated layers is directly related to the intergranular misorientation. To illustrate, we discuss in detail the interfacial structure at 90 degree-related grains. Boundaries in this system dissociate to form a 1 nm wide layer of material with close-packed planes arranged in the 9R stacking sequence (i.e., abc/bca/cab). Formation of this non-FCC layer can be understood by considering the distribution of Shockley partial dislocations that are intrinsic to the interface: separation of the pure-edge (90 degree) and mixed character (30 degree) dislocations, which are present in a ratio of 2:1, produces a stacking fault every third plane and a characteristic local plane bending. Finally, we discuss how this approach is generalized to other orientations by varying the ratio of dislocation types and how the constraints arising at boundary junctions affect the separation of the interfacial dislocations, and, thus, the boundary width. This work is supported by the U.S. Department of Energy under contract No. DE-AC04-94AL85000 in part by the Office of Basic Energy Science, Division of Materials Science.

**11:00 AM I8.9**

**INTERFACE-CONTROLLED CREEP DEFORMATION IN TWO-PHASE TiAl WITH ULTRAFINE LAMELLAR MICROSTRUCTURES.** Luke Hsiung, Lawrence Livermore National Laboratory, Chemistry and Materials Science Directorate, Livermore, CA.

Creep mechanisms of two-phase TiAl with ultrafine lamellar microstructures (gamma lamellae: 100-300 nm thick, alpha-two lamellae: 10-50 nm thick) at an intermediate-temperature range (650-810 C) have been investigated. A nearly linear creep behavior (i.e. the steady-state creep rate is nearly proportional to the applied stress) was observed under stresses below 300 MPa. Since the operation and multiplication of lattice dislocations within both gamma and alpha-two lamellae are very limited at a low stress level as a result of the refined lamellar spacing, creep mechanisms based upon glide and/or climb of lattice dislocations become insignificant, instead the mobility of interfacial dislocation arrays on lamellar interfaces becomes predominant. In this presentation, we will report the evidence to show that the mobility of interfacial dislocation arrays is primarily controlled by the impingement of lattice dislocations, and the diffusion of solute (impurity) segregation in lamellar interfaces. The nearly linear creep behavior observed at low-stress regime can be rationalized by the viscous glide of pre-existing interfacial dislocation arrays. According to this perception, we will demonstrate that the segregation of W to lamellar interfaces has a beneficial effect to the creep resistance of lamellar TiAl at the low-stress regime by decreasing the mobility of interfacial dislocations. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

**11:15 AM I8.10**

**ON THE SINK STRENGTH OF NANOSIZED GRAIN BOUNDARIES.** M. Samara, P.M. Derlet, H. Van Swygenhoven, and M. Victoria.

It is well known that grain boundaries (GB) act as sinks for interstitial atoms created during irradiation and that this results in a denuded zone around the GB. Experiments and modelling confirm this trend, showing a defect-free zone of about 3 to 20 nm around a discrete dislocation. Molecular dynamics simulations are performed to study defect production in irradiated nanocrystalline Ni with mean grain sizes of 5, 12 and 20 nm. It is shown that the interstitials are attracted to GBs by means of replacement collision sequences to these areas where misfit is accommodated by GB dislocations and excess free volume is present. Moreover, it is shown that stacking fault tetrahedra are easily formed in the nanosized grains, which would result in material hardening. The sink strength of GBs is investigated in terms of grain size and the non-equilibrium state of the GBs. (PRL 88(2002)125505, Phil. Mag. A 2002 in press)

**11:30 AM I8.11**

**PARALLEL GLIDE OF DISLOCATIONS IN ULTRATHIN COPPER FILMS.** T. John Balk, Gerhard Dehm and Eduard Arzt,

Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

Although it is well known that thin metal films exhibit mechanical properties significantly different from those of bulk metals, the underlying mechanisms responsible for these differences are not completely understood. In this study of thin film plasticity, the relationship between thermomechanical behavior and dislocation motion has been investigated in ultrathin, unpassivated copper films constrained by a silicon substrate. The stress-temperature behavior as determined from wafer curvature experiments has been directly compared to deformation microstructures observed during in-situ thermal cycling of plan-view specimens in the transmission electron microscope. The effects of film thickness on dislocation motion and on the evolution of flow stress in thin copper films will be presented. Wafer curvature experiments revealed that the room temperature flow stress rises nearly linearly with inverse film thickness, but then exhibits a plateau at approximately 650 MPa for films 400 nm and thinner. This plateau appears to result from the activation of a new deformation mechanism, which we have termed parallel glide, driven by diffusion along the surface and grain boundaries of the copper film. Unexpected dislocation activity on a (111) plane parallel to the film/substrate interface, which should experience no resolved shear stress, provides evidence for the occurrence of constrained diffusional creep in ultrathin films. This deformation process has been observed to be reversible during heating and cooling, and to be highly repeatable from one thermal cycle to the next. Moreover, the populations of parallel glide dislocations observed in the microstructure fully account for the plastic strains measured from wafer curvature experiments. Such observations are relevant to the largely unknown dynamical interactions between dislocations and the surface/interface, which are likely to increase in importance during the persistent miniaturization of thin film geometries.

11:45 AM **I9.12**

**THE ROLE OF GRAIN BOUNDARIES IN NANOCRYSTALLINE DEFORMATION.** Krystyn Van Vliet, Sedina Tsikata, and Subra Suresh, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

As grain boundaries comprise an increasing volume fraction of nanostructured metals and ceramics, the optimal design of these materials requires fundamental understanding of how grain boundary regions resist and accommodate permanent deformation. One outstanding issue in nanocrystalline mechanical behavior is whether a limit exists, beyond which further grain size refinement no longer increases the deformation resistance of the material. Despite considerable experimental and computational efforts, a general, atomistic description of how grain boundaries respond to large strains is lacking. Here, we present recent *in situ* experiments of nanocrystalline deformation under nanoscale contact, via the Bragg-Nye bubble raft model. This 2-D analogue to close-packed planes in face-centered cubic (FCC) crystals allows ready visualization and quantification of the effects of grain size, grain boundary orientation and loading profile (monotonic vs. cyclic) on large strain deformation. From these experiments, we observe a transition in both strength and accommodation mechanisms at a critical grain size. We compare these observations with new experiments and atomistic simulations in order to understand the role of imposed, local strain on the grain size at which this deformation transition is observed.

SESSION I9: CHARACTERIZATION OF NANOSTRUCTURED MATERIALS

Chair: Gan-Moog Chow

Wednesday Afternoon, December 4, 2002  
Room 312 (Hynes)

1:30 PM **\*I9.1**

(SUPER-)PLASTICITY OF NANOCRYSTALLINE MATERIALS.  
Horst Hahn and Karsten Albe, Technische Universität Darmstadt, Institute for Materials Science, Darmstadt, GERMANY.

From the beginning of research on nanocrystalline metals and ceramics the mechanical properties and in particular the (super-)plasticity of this novel class of materials have attracted much attention. This is due to the fact, that the strong grain size dependence of mechanical properties can lead to plastic behavior in brittle materials. There are many reports on mechanical properties of nanocrystalline metals, ceramics and composites. Some surprising results, i.e. the inverse Hall-Petch relationship observed in nanocrystalline metals and alloys, have led to the development of new theoretical models of the deformation processes of materials with nanometer sized grains, such as grain boundary sliding and planar interface formation. In addition, computer simulations have been employed substantially in the last few years to analyze the atomistic processes during deformation. In the talk the experimental results, the

phenomenological models and the results of computer simulations will be presented and compared critically.

2:00 PM **I9.2**

**STRUCTURE AND CHARACTERIZATION OF SOL-GEL AND AEROGL MATERIALS AND OXIDATION PRODUCTS FROM THE REACTION OF  $(CH_3O)_4Si$  AND  $C_{16}H_{33}Si(OCH_3)_3$ .** Thomas M. Tillotson and John G. Reynolds, University of California, Lawrence Livermore National Laboratory, Livermore, CA.

Reactions of  $(CH_3O)_4Si$  and  $C_{16}H_{33}Si(OCH_3)_3$  at various mole ratios were performed in methanol using base and acid catalysis. Sol-gel materials were formed that have low surface areas (approximately 10 m<sup>2</sup>/g). Subsequent supercritical drying using CO<sub>2</sub> at 40°C produced materials that are very different than traditional aerogels, with surface areas around the same values as the corresponding sol-gels, as well as no detectable meso-pore features. In some cases, the aerogels even melted upon heating. Spectroscopic characterization, using IR, <sup>29</sup>Si and <sup>13</sup>C NMR revealed normal Si-O substitution as well as incorporation of the carbon chain into the Si framework. Heating of the stable forms of the materials in air at different temperatures yielded, depending upon oxidation conditions, several materials with much higher surface areas, typical of aerogels. Pore size distribution measurements revealed meso-pore features with a narrow distribution around 35 Å. Spectroscopic characterization revealed the disappearance of the R-Si substitution and the appearance of a oxidized intermediate. This paper will describe the chemistry and characterization of these unusual sol-gels, aerogels, and oxidation products, as well as potential applications. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

2:15 PM **I9.3**

**STRAIN AND TEXTURE IN EQUAL-CHANNEL ANGULAR PRESSED ALUMINUM AND NICKEL.** Sven C. Vogel, Irene J. Beyerlein, Mark A.M. Bourke, Donald W. Brown, Carlos Tomé, Los Alamos National Laboratory, Los Alamos, NM, Bjørn Clausen, and Ersan Üstündag, California Institute of Technology, Pasadena, CA.

By using severe plastic deformation techniques such as equal channel angular pressing (ECAP), nano-structured metals with advantageous mechanical properties can be produced. Compared to the 'bottom-top' method of growing nano-crystals to obtain a nano-structured material, the 'top-bottom' approach of severely deforming a coarse grained material has the advantage that bulk, massive workpieces with 100% density and no cracks can be obtained. ECAPed metals and alloys can have very high yield strengths while high ductility is maintained, a unique and extremely attractive combination of properties. However, because of the implicitly large deformations, modeling and prediction of texture evolution and strain response is challenging. This talk will present results from a neutron diffraction study on aluminum and nickel samples that have been processed using the *B*<sub>2</sub> ECAP route, i.e. the sample is rotated by 90 degree between ECAP cycles. Specifically we report the evolution of the bulk texture and the hkl-dependent strain response post processing. The texture and strain results are discussed in the context of a visco-plastic self-consistent (VPSC) model and an elasto-plastic self-consistent (EPSC) model, respectively. The talk will address two subjects a) the viability of quantitative texture prediction using a VPSC model and b) the applicability of an EPSC model to a nano-scale refined grain structure.

2:30 PM **I9.4**

**RED SHIFT IN OPTICAL ABSORPTION TAIL AND SUPERPARAMAGNETISM OF GAMMA-Fe<sub>2</sub>O<sub>3</sub> NANOPARTICLES IN A POLYMER MATRIX.** John K. Vassiliou<sup>a</sup>, J. W. Otto<sup>b</sup>, A. Pothireddy<sup>a</sup> and J. J. Davis<sup>a</sup>; <sup>a</sup>Department of Physics, Villanova University, Villanova, PA, <sup>b</sup>Joint Research Center for the European Commission, Brussels, BELGIUM.

Well defined spherical particles of gamma-Fe<sub>2</sub>O<sub>3</sub> have been synthesized in the pores of a polymer matrix in the form of beads by an ion exchange and precipitation reaction. The particle size distribution is a gaussian with an average diameter of 80 Å. The DC magnetic susceptibility and the magnetization of the nanocomposite has been measured between 4 and 300 K using a Faraday balance and a magnetometer, respectively. The magnetic measurements demonstrate that the particles are superparamagnetic with a blocking temperature T<sub>b</sub> about 65 K. The optical absorption edge of the mesoscopic system is red shifted with respect to single crystal films of gamma-Fe<sub>2</sub>O<sub>3</sub> with an absorption tail extended deeply in the gap. Although lattice distortion and the existence of excitonic states in the gap can explain the absorption behavior, the red shift can successfully be explained by the quantum confinement of an electron-hole pair in a spherical well.

#### 2:45 PM I9.5

**NANOMECHANICAL CHARACTERIZATION ON ZINC AND TIN OXIDES NANOBELTS.** Minhua Zhao, Scott Mao, Univ of Pittsburgh, Dept of Mechanical Engineering, Pittsburgh, PA; Fengting Xu, John A. Barnard, Univ of Pittsburgh, Dept of Materials Science & Engineering, Pittsburgh, PA; and ZhongLin Wang, School of Materials Science & Engineering, George Institute of Technology, Atlanta, GA.

Beltlike (or ribbonlike) semiconducting zinc and tin oxides (so called nanobelts) were successfully synthesized by simply evaporating the desired commercial metal oxide powders at high temperatures without the presence of catalyst. The morphology and nanomechanical behavior of the nanobelts were characterized by digital Instruments Nanoscope IIIa AFM and Hysitron TriboScope with homemade sidewise CCD camera. Morphology analysis shows the nanobelts have a rectanglelike cross section with typical widths of several hundred nanometers, widths-to-thickness ratios of 5 to 10, and lengths of hundreds of micron meters. An indentation probe with the tip radius  $< 25\text{nm}$  was used in tapping mode AFM, while a cubic corner tip with the radius  $< 40\text{nm}$  was employed in STM mode TriboScope. The results derived by AFM and TriboScope were compared. It was shown that tapping mode AFM gave a better image quality in morphology and much higher value of hardness than that of STM mode TriboScope. The reason of the later case lies in the difference of tip radius, which was briefly discussed by using strain gradient plasticity theory. In addition, indentation size effect was revealed for the nanobelts in the indentation depth smaller than 50nm. The difference in zinc and tin oxides was presented.

#### 3:30 PM I9.6

**ANOMALOUS X-RAY SCATTERING FOR DETERMINATION OF NANOSTRUCTURED ALLOY FORMATION AND SITE-SPECIFIC CHEMISTRY OF BRAGG PEAK.** G.M. Chow, Dept of Materials Science, National University of Singapore, SINGAPORE.

Structural characterization of alloys by conventional x-ray scattering has been well established. For coarse-grained materials, the appearance of a single set of diffraction peaks and disappearance of elemental peaks are commonly accepted as evidence of formation of a solid solution. The variation of lattice parameter with alloy composition can be qualitatively followed using Vergard's law. However, when the crystallite size of a nanostructured material is reduced to below a critical length scale, conventional x-ray diffraction fails to provide correct information on alloying of elements with close lattice parameters, even for elements commonly accepted to have miscibility. In this talk, we show by using anomalous scattering, nanostructured NiCo films did not necessarily form solid solution as expected from their phase diagram or suggested by the results of conventional x-ray diffraction [1]. The elemental composition of the textured diffraction peak of CoCrPt has also been investigated using this method [2]. The limitations of using conventional x-ray scattering alone for studying nanostructured alloys are discussed. Advantages of complementary structural investigations using anomalous x-ray scattering (for long range order) and extended x-ray absorption fine structure spectroscopy (for short range order) are presented. The limitations of applying conventional phase diagram to nanostructured materials are also addressed [3]. References: [1] Applied Physics Letters, 75:2503 (1999). [2] Applied Physics Letters, 80:1607 (2002). [3] Materials Science and Engineering B, in press. This work was supported by the National University of Singapore and the Office of Naval Research, USA.

#### 4:00 PM I9.7

**INTERRELATIONSHIP BETWEEN ATOMIC SPECIES, BIAS VOLTAGE, TEXTURE AND MICROSTRUCTURE OF NANO-SCALE MULTILAYERS.** D.B. Lewis, Q. Luo, Materials Research Institute, Sheffield Hallam University, Sheffield, UNITED KINGDOM; Z. Zhao, Department of Engineering Materials, The University of Sheffield, Sheffield, UNITED KINGDOM; G. Nayal, P. Eh. Hovsepian, and W.-D. Münz, Materials Research Institute, Sheffield Hallam University, Sheffield, UNITED KINGDOM.

A matrix of binary and ternary nitrides containing lighter elements (Al, Ti, V and Cr) with atomic mass  $< 52$  and heavier elements (Y, Zr, Nb and W) with atomic mass  $> 89$  have been formulated. These have been grown as multilayer coatings (bi-layer thickness  $\sim 3.0\text{ nm}$ ) on stainless steel substrates using an industrial size multiple target ABS coater. When lighter elements are incorporated into the multilayer at a lower bias voltage ( $U_B = -75\text{ V}$ ) pronounced  $\{111\}$  or  $\{110\}$  textures develop which are determined by the dominating species present. A  $\{111\}$  or  $\{110\}$  texture develops when TiAlN or VN dominates the matrix respectively. In contrast when a heavier element is incorporated a  $\{100\}$  texture is observed. Additionally there is a strong indication that in the case when heavy elements ( $> 89$ ) are involved in the growth process an incoherent type of lattice evolves. Conversely, when only light elements ( $< 52$ ) are involved in the growth process a coherent lattice evolves. This observation is limited

only for the lower bias voltage range of  $U_B = -75$  to  $-100\text{ V}$ . However, as the bias voltage is increased (up to  $U_B = -150\text{ V}$ ) the texture becomes increasingly sharp and in all cases a  $\{111\}$  texture develops. A lower residual compressive stress (typically  $-2.0\text{ GPa}$ ) is observed when one of the bi-layers is dominated by a heavier element. The stress increases (up to  $10\text{ GPa}$ ) in these coatings when the bias voltage is increased thus reaching similar values to coatings containing nitrides of only light elements. In parallel this results in an increase in plastic hardness ( $80\text{ GPa}$ ) and the sliding wear coefficient by an order of magnitude regardless of the type of lattice growth observed. The tribological results are supported by the first field milling tests on TiAlN based coatings.

#### 4:15 PM I9.8

**CHARACTERIZATION OF LARGE DEFORMATION FIELD IN ULTRA-FINE GRAINED MACHINING CHIPS.** Renae F. Kezar, Travis L. Brown, Srinivasan Swaminathan, W. Dale Compton and Srinivasan Chandrasekar, Center for Materials Processing and Tribology, School of Industrial Engineering, Purdue University, West Lafayette, IN.

It has been known for sometime that significant benefits can be gained by deforming metals to very large plastic strains. Principal among these are microstructure refinement, and enhanced mechanical and physical properties. Of significant current interest is the use of severe plastic deformation to produce bulk solids with ultra-fine grained microstructure. The general experimental approach that has been used to impose large plastic strains is multi-stage deformation using processes such as extrusion, rolling, and drawing. Here, we show that the process of chip formation in 2-D, plane strain machining provides a simple experimental configuration, in which the effects of very large strain deformation on microstructure and mechanical properties can be systematically studied using just one stage of deformation. A series of experiments have been carried out on 2-D, plane strain machining of copper and iron using a hard wedge indenter (tool) at low velocity. The deformation field associated with chip formation is studied using a specially devised experimental configuration in which a partially formed chip, that is not yet separated from the bulk of the material, is created. Nano-indentation, transmission electron microscopy and atomic force microscopy, have been used to characterize the shape, extent and properties of the deformation field and its dependence on the geometry of the tool. The hardness and the microstructure in the deformation field have been directly measured and correlated. The characteristics of the deformation field are shown to be strikingly similar to those prevailing in a process such as equal channel angular extrusion. Finally, it is shown that microstructure refinement by machining is significant, resulting in chips with sub-micron sized grain structures.

#### 4:30 PM I9.9

**ATOMIC-RESOLUTION Z-CONTRAST STEM STUDY OF A HIGH-STRENGTH NANOCRYSTALLINE  $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$  ALLOY.** Eiji Abe, National Institute for Materials Science, Tsukuba, JAPAN; Y. Kawamura, Dept of Mechanical Engineering and Materials Science, Kumamoto University, Kumamoto, JAPAN; A. Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Recently, it has been shown that a nanocrystalline  $\text{Mg-1at.\%Zn-2at.\%Y}$  alloy, prepared by warm extrusion rapidly solidified powders at  $573\text{K}$ , reveals excellent mechanical properties including maximum tensile yield strength  $\sim 600\text{MPa}$  and elongation  $\sim 5\%$  at room temperature [1, 2]. In the present paper, we investigate the microstructure of the nanocrystalline  $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$  alloy systematically from a micron scale to an atomic scale using TEM, particularly focusing on the distributions of Zn and Y in the structure. We employ a unique atomic-resolution high-angle annular dark field scanning-TEM (HAADF-STEM) by which the relatively heavy atom positions emerge out with highlighted contrast in the image due to the Z(atomic number)-contrast. Consequently, we find a significant distribution of Zn and Y in the microstructure, with the aid of nano-probe EDS analysis. That is, some grains revealed striking bright Z-contrasts in a very fine lamellar fashion, directly representing that Zn and Y atoms are located not randomly as a solid solution but at the specific positions in the lamellar structure (chemical order). These features are attributed to the formation of a novel long-period ordered structure, whose unit cell is composed of six close-packed planes of the magnesium crystal with a stacking sequence of ABCBCB' where A and B' layers are significantly enriched by Zn and Y [3]. The lattice is distorted from an ideal hexagonal lattice of 6H-type (ABCBCB), which is likely due to an asymmetry of the chemical order with respect to the 6H-type structure. The present results demonstrate that additional elements of a few atomic percent to Mg lead to formation of a long-period chemical-ordered as well as stacking-ordered structure, as directly revealed by a unique Z-contrast method. The formation of the present long-period ordered structure from the Mg solid solution with a hexagonal close-packed (hcp) structure is briefly discussed. [1] Kawamura et al, Mater Trans 42

**4:45 PM I10.10**

**PLASTICITY OF EPITAXIAL Al THIN FILMS.** Gerhard Dehm, T. John Balk, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY; and Beverley J. Inkson, Department of Materials, University of Oxford, UNITED KINGDOM.

Many previous thin-film studies are complicated by the superposition of film thickness and grain size effects on mechanical behavior. However, fundamental information regarding the influence of thickness constraints on plasticity mechanisms in thin metal films, excluding contributions of grain size and grain orientation, can be obtained using epitaxial metal films. For this purpose, Al films were magnetron sputtered onto (0001) oriented  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates, resulting in a (111) Al || (0001)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $<1-10>$  Al ||  $<10-10>$   $\alpha$ -Al<sub>2</sub>O<sub>3</sub> heteroepitaxial orientation relationship that consists of two twin-related Al variants. Films with thicknesses ranging from 100 to 2000 nm were thermally cycled between room temperature and 400°C, and film stresses were measured using a laser scanning technique. Both the biaxial compressive flow stresses at 400°C and the biaxial tensile flow stresses at 40°C increase with decreasing film thickness. The flow stresses are in agreement with predictions of the Nix-Freund model. However, for film thicknesses exceeding 350 nm, the decreasing flow stresses are better reproduced by a Hall-Petch model, suggesting a transition in dislocation mechanisms. Stress relaxation measurements performed at 150°C during cooling imply dislocation pinning distances that are 5 to 10% of the film thickness. These findings are compared to textured Al films and discussed in light of TEM observations.

**SESSION I10: SYNTHESIS OF NANOSTRUCTURED MATERIALS - I**

Chair: Thomas Tsakalakos  
Thursday Morning, December 5, 2002  
Room 312 (Hynes)

**8:30 AM I10.1**

**A LOW-COST MANUFACTURING PROCESS FOR NANOSTRUCTURED MATERIALS.** Srinivasan Swaminathan, Travis L. Brown, Srinivasan Chandrasekar, W. Dale Compton, Alexander H. King, and Kevin P. Trumble, Schools of Engineering, Purdue University, West Lafayette, IN.

A novel method of making nano-structured metals and alloys is described. The method involves subjecting a material to large scale deformation using the process of machining. The chips produced during lathe machining of a variety of pure metals, steels and other alloys are shown to be nano-structured with grain (crystal) sizes in the range of 100 to 800 nanometers. The hardness of the chips is found to be significantly greater than that of the bulk material. An annealing study has been carried out to determine the range of temperatures over which these structures are stable and retain their mechanical properties. The characteristics of these nano-structured materials are found to be strikingly similar to those produced by severe plastic deformation processes. The observations provide clear evidence that nano-structured metals and alloys can be produced through the normal metal removal processes, such as lathe machining. Perhaps more importantly, this method provides an avenue for the production of nano-crystalline structures in a far wider group of materials and at far lower costs than has been foreseen using other processes. It is quite likely that the enormous quantities of chips generated in industrial machining operations, which are currently disposed of as scrap metal, are all composed of ultra-fine grained structures. The benefits associated with re-utilization of these chips should also be significant.

**8:45 AM I10.2**

**A NOVEL FABRICATION METHOD TO GENERATE LARGE AREA PERIODIC NANOSTRUCTURES.** Woo Lee, Won-Cheol Yoo, Mi-Kyoung Jin, and Jin-Kyu Lee, School of Chemistry and Molecular Engineering, Seoul National University, Seoul, KOREA.

Recently we have developed a novel non-lithographic route to fabricate various nanostructures with large area. This method involves in the utilization of electrochemically prepared textured aluminum sheets or nanoporous anodic aluminum oxide (AAO) as a replication master, in conjunction with our newly developed spin-on assisted replica molding of polymers and nanoparticles, and electrochemical deposition of metals. Multiple copies of two-dimensional vast arrays of nano-lenses, nano-posts, and polymer/nanoparticle composites with feature sizes ranging from 30 to 400 nm, could be easily obtained by this novel method. TEM, FE-SEM, and AFM analyses revealed that the present nanofabrication technique offers highly facile and economic way for the production of large area periodic nanostructures

with high fidelity in pattern transfer as well as with a good degree of flexibility in materials. In addition, the method has several advantages over conventional lithographic techniques.

**9:00 AM I10.3**

**FABRICATION OF FERROELECTRIC NANO-STRUCTURES.** M. Alexe, S. Bhattacharya and U. Gösele, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

In this report, we have explored the possibilities of the fabrication and characterization of the ferroelectric nano-structures by various methods. Techniques included direct e-beam lithography and the self-assembly technique. A generalized chemical route to prepare isolated nano particles was also sought. For the patterns prepared by the e-beam technique, it was seen that, there could be a strong coupling between two closely spaced nano elements. The spacing between them was found to be the key factor in manipulating the dimension of them, i.e., whether it would be a rod-like pattern or a two dimensional array of isolated squares or circles. The shape of individual nano-elements was dependent on the processing route, i.e., the heat treatment and also the orientation of the substrate. The choice of the electron beam sensitive precursor was also very important in determining the final size of the memory cells, which were of the order of 50-100 nm. The studies indicated that a further decrease in size would be possible by choosing the appropriate precursor concentration and the electron beam intensity. Alternatively, we have also tried to fabricate a self-assembled nano pattern by utilizing the crystal field of the substrate itself. The chemical route, which adopted the microemulsion-mediated synthesis, appeared to be very encouraging for producing very small monodisperse nano particles and powders, with sizes of 10-60 nm. The possibility to form a two dimensional arrangement of these micro droplets was explored with a suitable choice of the substrate material, and the method of the coating. Further studies are in progress in understanding the structural and the electrical properties of an individual nano cell as well as of a collection of them.

**9:15 AM I10.4**

**FORMATION, MECHANICAL AND ELECTRICAL PROPERTIES OF Ni-BASED AMORPHOUS ALLOYS AND THEIR NANOCRYSTALLINE STRUCTURE.** Xiangcheng Sun, Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, AL; Tiemin Zhao, Institute of Metal Research, Chinese Academy of Science, Shenyang, P.R. CHINA.

One new Ni-based amorphous alloy in Ni<sub>60</sub>Ti<sub>20</sub>Zr<sub>20</sub> system exhibiting a wide supercooled liquid region before crystallization has been prepared by melting spinning. The glass transition temperature ( $T_g$ ) is as high as about 723K, the supercooled liquid region reaches  $\Delta T_g = 97K$  ( $\Delta T_g = T_g - T_c$ ,  $T_c$  crystallization temperature), and high reduced glass transition temperature ( $T_g/T_m$ ) of 0.57. Besides, the amorphous alloys exhibit a high tensile strength ( $\sigma_{UTS}$ ) with 1015 MPa at room temperature. The electrical conductivity within the temperature ranges of 15K < T < 300K have been measured for this amorphous alloy, it is observed that the conductivity obeys a  $T^{1/2}$  law, which can be explained by electron-electron interaction model. On the other hand, after primary crystallization by annealing this amorphous alloy, nanocrystalline composites formation has been observed by in-situ transmission electron microscopy (TEM). Both the analysis of the x-ray diffraction (XRD) and the selected area electron diffraction patterns (SAED) give the evidence of metastable Ti<sub>2</sub>Ni and Zr<sub>2</sub>Ni nanophases in these nanocrystalline composites. It implied that the microstructure after the primary crystallization consists of the nanocrystals less than 15 nm in size embedded in the amorphous matrix.

**9:30 AM I10.5**

**GROWTH AND ANOMALOUS LOW-TEMPERATURE ELECTRICAL CHARACTERISTICS OF NANO-STRUCTURED NiAl FILMS.** Ashutosh Tiwari, A. Chugh, H. Wang, and J. Narayan, Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC.

We have grown nano-structured NiAl films on silicon substrates by using a pulsed laser deposition technique with grain size ranging from 5 nm-500 nm. Films were characterized by X-ray diffraction, transmission electron microscopy and high resolution electrical resistivity measurements. Low temperature electrical resistivity of nano-structured NiAl films shows anomalous electrical characteristics, which strongly depends on grain-size. It has been found that while poly-crystalline NiAl shows a metallic behavior with positive temperature coefficient of resistivity (TCR) in the temperature range 12K-300K, the TCR of nano-structured specimens show a sign reversal with a positive value at room temperature and a negative one at lower temperatures. Enhanced electronic correlation effects are found to be responsible for the low temperature electrical-resistivity behavior of the system.

**9:45 AM I10.6**

**HIGH STRENGTH SILICON DIOXIDE AEROGELS.** Benjamin L. Lawson, Taofang Zeng, North Carolina State University, Dept of Mechanical and Aerospace Engineering, Raleigh, NC.

Silica aerogels, mostly made of mesopores, are sol-gels that are supercritically dried to form an incredibly lightweight, thermally unreactive, yet brittle material. Remarkable steps have been taken to control the properties of aerogels at the nanometer level such as controlling the surface area, density, pore volume, and pore size distribution via different sol-gel and supercritical drying processes. Still, aerogels remain brittle and delicate. Creating an aerogel with a nearly uniform pore size distribution would greatly enhance its mechanical properties. This study proposes a new method to improve the mechanical strength. Through the addition of a specific inorganic conglomerate to the sol-gel process, the pore size of silica aerogels can be fine tuned with a uniform pore size distribution. The enhanced backbone of the aerogels and the more uniform pore size distribution greatly increase the mechanical strength of the aerogels.

**10:30 AM I10.7**

**NON-STRUCTURED BULK POLYCRYSTALLINE CERAMICS FABRICATED BY RAPID SOLIDIFICATION OF EUTECTIC MELTS.** Masahiro Yoshimura, Shunji Araki, and Jose M. Calderon-Moreno, Tokyo Institute of Technology, Center for Materials Design, Materials and Structured Laboratory, Yokohama, JAPAN.

Nano-structured bulk ceramics have generally been fabricated by sophisticated sintering processes using carefully prepared fine powders or nano-particles. These powder/shaping/sintering processes take multi-steps thus consume long times and a lot of energies even though they consume much less than so-called "high-tech." processes where highly energetic species like vapors, gases, molecules, atoms and/or ions are used as reactants in sophisticated equipments like sputtering, vaporization, PVD, CVD, etc. using microwave, beam, plasma etc. in vacuum chambers or even in clean rooms. We are challenging to fabricate polycrystalline ceramics by powderless, fireless and vacuumless processes. In addition to "Soft Solution Processing" which targets direct fabrication of shaped ceramics in solutions [1-2], we have studied melt/solidification methods [3-4], which target also direct fabrication of shaped ceramics. In contrast of many studies in metallic systems, few studies on melt/solidification have been done in ceramic systems except for glasses and glass-related systems. It has been believed that melt/solidified ceramics would crack during cooling due to the brittle nature of ceramic materials and the accumulation of residual stresses. In order to eliminate the stress accumulation, we have selected rapid solidification of eutectic melts, which would produce dense polycrystalline ceramics with finer grains of multi-phases. We have succeeded to fabricate nano-structured bulk ceramics in the ternary systems:  $\text{Al}_2\text{O}_3$ - $\text{Y}_3\text{Al}_5\text{O}_12$  (YAG)- $\text{ZrO}_2$ ,  $\text{-HfO}_2$ , or  $\text{Al}_2\text{O}_3$ - $\text{GdAlO}_3$ - $\text{ZrO}_2$ , which consisted of constituent oxide grains with 20-50 nm in size. Translucent/transparent bulk ceramics could be obtained in particular samples. Their unique nano-/micro-structures and properties have been studied. Those nano-structured bulk ceramics may be useful for many structural applications as well as functional applications. Ref. 1) M. Yoshimura et al., MRS Bulletin, special issue of Soft Processing, vol. 25 (Sept. 2000) 2) M. Yoshimura, Key Eng. Mater. 206-213, pp. xv-xx (2001) 3) M. Yoshimura et al., J. Mater. Sci. Lett., 4 1082 (1985) 4) J.M. Calderon and M. Yoshimura, Solid State Ionics, 141-142, 343 (2001)

**10:45 AM I10.8**

**NOVEL NANOSTRUCTURED THIN FILMS.** Igor Haurilay, Joint Stock Company "ALAMEX", Minsk, BELARUS; Alexander Govyadov, Peter Mardilovich, recently Hewlett-Packard, Corvallis, OR; and Yuval C. Avniel, MicroPowder Solutions, LLC, Longmont, CO.

This paper describes a new deposition technology capable of producing ultra thin engineered nanostructured coatings from a wide variety of materials. The underlying principle of the technology leverages the natural mechanisms of stress reduction in thin films and the mutual affinity of film components and substrates to produce predetermined structures. The technology is implemented by consecutively depositing materials at proper conditions to produce 3D anisotropic structures on a nanometer to sub-micron scale. The structure formed is a function of the deposition parameters of each individual component. By varying deposition conditions, one can produce a plethora of geometries with different system chemistries. As an example, an electro-conductive nanostructured hetero-phase film with superior wear resistance was prepared and is discussed in detail. The technology enables enhancement of optical, electro-magnetic, mechanical and combinatorial properties. Applications include wear resistant, conductive, optical and decorative thin films; strength enhanced coatings, abrasive media, optical coatings with 3D anisotropy, nanodimensional templates, oriented magnetic storage media, and quantum dot arrays.

**11:00 AM I10.9**

**SYNTHESSES AND CHARACTERIZATION OF NOVEL VANADIUM OXIDE NANOTUBES AND NANOFIBERS.**

Samuel Lutta, Peter Y. Zavalij, and M. Stanley Whittingham, State University of New York at Binghamton, Institute for Materials Research and Dept of Chemistry, Binghamton, NY.

We are exploring the synthesis and properties of vanadium oxide nanotubes and nanofibers. Nanotubes initially formed with surfactant templates have been readily exchanged with simple cations without change of the basal-plane structure. These compounds contain  $\delta$ -like vanadium oxide layers, with the vanadium in  $\text{VO}_6$  octahedra. This structure is particularly suitable for redox reactions. A new method has been developed to produce vanadium oxide nanofibers with diameters in the 40 nm to 130 nm range and lengths up to a few microns. This method could be of great interest for production of 1D metal oxide materials and thin films. The fibers have been characterized by SEM, TEM, XRD, TGA, FTIR and DCP-AES. This work is being supported by NSF DMR9810198.

**11:15 AM I10.10**

**PROCESSING OF HIGH-STRENGTH NANOCRYSTALLINE FeCo INTERMETALLIC MATERIAL.** A. Duckham, D. Zhang, C.H. Shang, D. Liang<sup>a</sup>, R.C. Cammarata, R.L. Lheny<sup>a</sup>, C.L. Chien<sup>a</sup>, and T.P. Weihs, Department of Materials Science and Engineering;

<sup>a</sup>Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, MD.

We describe a conventional thermo-mechanical process for fabricating nanocrystalline intermetallic materials that are both very strong (>2GPa) and reasonably ductile ( $\geq 3\%$ ) in tension. Unlike more traditional methods of fabricating nanocrystalline materials, such as powder processing, our process results in a fully dense, defect free material. The method consists of controlled, low temperature annealing of FeCo alloys following large amounts of deformation through cold rolling. Grain sizes have been measured by transmission electron microscopy (TEM) to be as low as 100 nm, compared to the much larger grain structures ( $> 1 \mu\text{m}$ ) that result after standard industrial anneals at higher temperatures. We have investigated the role that the related processes of recovery, recrystallization and reordering have on the formation of the nanocrystalline grain structures during annealing. We have employed differential scanning calorimetry (DSC) to better understand the relative extent of these processes and neutron scattering in order to quantify the amount of ordering as a function of annealing conditions. FeCo alloys are the materials of choice for the fabrication of soft magnetic components used in jet engines. However, this very high yield strength with appreciable ductility ranks this material as one of the strongest and most useful for many structural applications.

**11:30 AM I10.11**

**SILVER NANODISK: SYNTHESIS, CHARACTERIZATION AND SELF-ASSEMBLY.** Sihai Chen, Zhiyong Fan, and David L. Carroll, Clemson Univ, School of Materials Science and Engineering, Clemson, SC.

A new form of silver nanostructured materials, i.e., silver nanodisk, is generated by a solution-phase approach. In this method, two main steps are applied: the first is the generation of the truncated triangular silver nanoplates, which are obtained by seed-mediated growth of silver particles using cetyltrimethylammonium bromide (CTAB) as the soft templates. The second is the mild aging of the above triangular silver nanoplate solution at 40°C to get the desired silver nanodisks. Transmission electron microscopy and atomic force microscopy studies show that the nanodisk has a thickness of the order of 20 - 30 nm, and a diameter around 60 nm. X-ray and electron diffraction analysis reveal that the nanodisk is single crystal and with its basal plane as (111) lattice plane. These nanodisks display a strong surface plasmon absorption band at 475 nm; this band can be continuously tuned within 420 nm to 560 nm through adjusting the aging time. The formation of self-assembled monolayer of CTAB on the basal plane is suggested to account for both the anisotropic growth from triangular nanoplates to nanodisks, and the formation of large-scale necklace-like structures.

**11:45 AM I10.12**

**SYNTHESIS AND CHARACTERIZATION OF ALLYLESTER AND LAYERED SILICATE CLAY NANOCOMPOSITE.** Wansoo Huh, Barry Farmer, Richard Vais, Air Force Research Laboratory, MLBP, WPAFB, OH; Sang-Won Lee, and Se-Woong Pang, Dept of Chem & Environ Eng, Seoul, KOREA.

Allylester is known to be the high performance thermoset polymer with superior thermal resistance and excellent wear resistance. It can be synthesized by transesterification reaction of prepolymer, which is made of diallyl ester monomer and diol with peroxide radical initiator.

In this study, allylester prepolymer has been obtained by dially terephthalate and 1,3-butane diol with monobutyltin oxide catalyst. Nanocomposite of allylester and organophilic layered silicate Montmorillonite was prepared by melt-intercalation method as well as in-situ polymerization. The effect of clay content, clay type, processing method and processing conditions on the degree of clay dispersion in allylester matrix has been studied. The thermal and mechanical properties of prepared nanocomposite depend on the degree of dispersion of clay in allylester matrix. From XRD results, it was found that in-situ polymerization shows better exfoliation behavior compared with melt intercalation method using mechanical stirring or ultrasonic process. The results of curing mechanism effect on the dispersion of clay are to be presented.

#### SESSION I11: SYNTHESIS OF NANOSTRUCTURED MATERIALS - II

Chairs: Sudipta Seal and Ganesh Skandan  
Thursday Afternoon, December 5, 2002  
Room 312 (Hynes)

##### 1:30 PM I11.1

#### SYNTHESIS AND CONSOLIDATION OF NANOPARTICLES TO PREPARE NANOCOMPOSITE COMPONENTS. S. Wannaparhun, S.C. Kurty, E. Megen, S. Patil and S. Seal, AMPAC and MMAE, University of Central Florida, Orlando, FL.

Nanocomposite ceramic materials have potential applications where enhanced strength, stiffness and fracture toughness with excellent high temperature properties are the major criteria for materials selection. The objective of the present work was to synthesize various metallic and oxide nanoparticles including Ni and alumina using sol-gel and microemulsion techniques. These nanoparticles are further characterized using XPS, HRTEM, XRD and SEM analyses for their chemical state, size distribution, shape and various phases present. Subsequently, these nanoparticles were consolidated using Laser, Plasma and hot isostatic press (HIP) processes to yield bulk nanocomposite components. The study revealed comparative consolidation behaviour of these nanoparticles among three processes.

##### 1:45 PM I11.2

#### SYNTHESIS OF HIGH ASPECT RATIO Ag/Pt

NANOSTRUCTURES WITH THE RADIOLYSIS METHOD. C.M. Doudna, M.F. Bertino, University of Missouri-Rolla, Department of Physics; F. Blum, University of Missouri-Rolla, Department of Chemistry; A. Tokuhiro, University of Missouri-Rolla, Department of Nuclear Engineering; P. Fraundorf, University of Missouri-St. Louis, Department of Physics and Astronomy; Debdutta Lahiri Dey, Bruce A. Bunker, University of Notre Dame, Physics Department; Jeff Terry, and Soma Chattopahay, Illinois Institute of Technology, Biological, Chemical, and Physical Sciences.

We present a technique to synthesize high aspect ratio metallic nanostructures based on the radiolysis method. In our experiments, we irradiate with gamma rays aqueous solutions containing mixtures of Ag and Pt ions, and a water-soluble polymer. The aspect ratio of the nanoparticles is controlled by varying radiation dose rate, type of polymer, and type of counterions. Transmission electron microscopy shows that wire-like structures composed by grains with fcc structure can be formed with a length of up to 3.5  $\mu$ m, and typical diameters between 5 and 12 nm. X-Ray Absorption Spectroscopy (XAS) shows that Ag and Pt do not form an alloy, but remain segregated. Our results are compared with previous nanoparticle synthesis carried out with the radiolysis method, and with more recent experiments, where wet chemistry techniques were employed to synthesize noble metal nanowires.

##### 2:00 PM I11.3

#### MECHANICAL AND STRUCTURAL INVESTIGATION OF HIGHLY ALIGNED SINGLE-WALLED CARBON NANOTUBES IN POLYMER COMPOSITES. Reto Haggemueller, Wei Zhou, John E. Fischer and Karen I. Winey, University of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA.

Single-walled carbon nanotubes (SWNTs) have demonstrated far superior mechanical, thermal and electrical properties relative to carbon fibers. Similar properties are expected for SWNT/polymer nanocomposites. We have efficiently dispersed SWNTs in polystyrene (PS) and polyethylene (PE) using a twin screw compounding. PE composites were melt spun into fibers to achieve highly aligned nanotubes. Polarized Raman spectroscopy shows that the alignment increases with decreasing fiber diameter but decreases with increasing nanotube loading. Mechanical properties increase with better alignment and higher nanotube loading. The elastic modulus increases up to 450% relative to PE fibers for 20wt% nanotube loading at an intermediate fiber diameter of 100  $\mu$ m. Thermal properties of aligned

SWNT/PE composites are measured. The dispersion of nanotubes in thermoplastics is investigated by scattering methods.

##### 2:15 PM I11.4

#### DEFORMATION-STRUCTURE RELATIONSHIPS OF CARBON NANOTUBES FILLED THERMOPLASTIC ELASTOMERS. Hilmar Koerner, Chyi-Shan Wang, University of Dayton Research Institute, Dayton, OH; Richard A. Vaia, Max D. Alexander, Nathan A. Pearce, Heather Bentley, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH; Benjamin S. Hsiao, Igor Sics, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY; and Dale W. Schaefer, Materials Science and Engineering Department, University of Cincinnati, Cincinnati, OH.

The promising mechanical and electronic properties of carbon nanotubes filled polymers, which are mostly governed by morphological parameters such as diameter, length and orientation lead to a growing interest in the design of future generation conducting nanocomposites. However, realization of the potential advantages still presents a large number of experimental and practical challenges. Performance requirements necessitate the development of systematic structure-property relationships. To begin to develop these relationships this effort utilizes simultaneous tensile/real-time synchrotron X-ray studies and supplementary DMA measurements to investigate the synergism of orientation of nanotubes, hard and soft segments of the elastomer and the effect of carbon nanotubes on dynamic deformation, strain hardening, creep and crystallization of elastomer composites. The observations provide insight into the strain-dependent mechanical and electrical properties of these nanocomposites.

##### 2:30 PM I11.5

#### FABRICATION AND CHARACTERIZATION OF WATER-BORN MULTIWALL NANOTUBE NANOCOMPOSITE FILMS AND COATINGS. Max D. Alexander, Jr., Chyi-Shan Wang, Heather J. Bentley, William Click and Hilmar Koerner, Air Force Research Laboratory, Wright-Patterson AFB, OH.

The fabrication of water-born nanocomposites containing multi-wall nanotubes has presented a significant technical challenge. Currently, these materials are formed by strong acid treatment of the nanotubes. This treatment can result in significant shortening of the tubes and degradation of the resulting mechanical and electrical transport properties. Here we present an alternate technique in which various conducting and non-conductive water-soluble polymers are physi-adsorbed to the surface of the nanotube. These interactions with the nanotubes result in highly uniform suspensions of water-based urethane coatings and bulk materials. We will examine the morphology of these nanostructured materials and the resulting thermal, electrical and mechanical properties.

##### 2:45 PM I11.6

#### FLUORINATED SINGLE WALL NANOTUBE/POLYETHYLENE COMPOSITES FOR MULTIFUNCTIONAL RADIATION PROTECTION. M.X. Pulikkathara, R. Wilkins, Center for Applied Radiation Research, Prairie View A&M University, Prairie View, TX; Meisha Shofner, Jerry Vera, Enrique V. Barrera, Department of Mechanical Engineering and Material Science, Rice University, Houston, TX; Fernando Rodriguez-Macias, Department of Chemistry, Rice University, Houston, TX; R. Vaideyanathan, C. Green, and C. Condon, Advanced Ceramics Research, Tucson, AZ.

Fluorinated Single Wall Nanotubes (f-SWNTs) have been processed in polyethylene by an incipient wetting technique to achieve a well dispersed nanocomposite for radiation protection/structural dual use. In some cases, samples were further processed using the rapid prototyping method of fused deposition modeling. f-SWNTs are seen as a near term approach for achieving un-roped nanotubes for composite applications. Fluorination leads to the separation of the roped nanotubes and may even shorten the tube lengths. Composites were exposed to 40 MeV proton radiation with a flux of about  $1.7 \times 10^7$  p/cm<sup>2</sup>/sec to a total fluence of  $3 \times 10^{10}$  p/cm<sup>2</sup>. This exposure is consistent with a long-term space mission in low earth orbit. The samples were evaluated by means of Raman Spectroscopy, TGA, and tensile tests. These results were compared to the unexposed composite and unfilled polymer samples. It is expected that nanotube polymer composites will be effective radiation protection shielding when prepared to contain hydrogen. This study has focused on the stability of the nanotube composites when exposed to radiation and prior to hydrogen exposure. It was shown that the composites maintained their mechanical integrity after irradiation and that no visible damage was observed from microscopy study. This work has been partially supported by the NASA SBIR No. NAS1-02001 and NASA Grant No. NCC 9-114. M. X. Pulikkathara is a NASA Harriett G. Jenkins Fellow and Meisha Shofner is supported by a NSF Graduate Fellowship. A portion of this work was supported by the Welch Foundation Grant No. C-1494.

**3:30 PM I11.7**

**GROWTH OF CARBON NANOTUBES ON CATALYST NANOPARTICLES PREPARED BY NI ION IMPLANTATION INTO Si AND SiO<sub>2</sub>.** A.R. Adhikari, M.B. Huang Department of Physics, University at Albany-State University of New York, Albany, NY; B.Q. Wei, R. Vajtai, and P.M. Ajayan, Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

Chemical vapor deposition (CVD) is the most versatile method for producing carbon nanotubes (CNTs), one of the most auspicious materials for nanomechanics and nanoelectronics. The growth process strongly depends on the properties (size, location, density etc.) of catalysts particles and their interactions with substrates. In this work, we investigated the role of catalyst nanoparticles prepared by ion implantation in the CVD growth of CNTs. As the first step, Ni ions of energy 100 keV were implanted into Si and SiO<sub>2</sub> substrates, resulting in a projected range of ~75 and 100 nm, respectively. The implanted doses of Ni were varied between 2e15 - 1e17 cm<sup>-2</sup>. Post-implantation annealing around 1000°C produced nanometer crystallites of Ni in SiO<sub>2</sub> and nickel silicide in Si, with their size distributing in the range of 5-20 nm, depending on the implanted doses. As the second step, CNTs were grown on these substrates containing catalyst nanoparticles, by CVD through decomposition of hydrocarbon. The morphology and property of the resultant CNTs were examined with various techniques including transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). We discuss the effects of different parameters, e.g., the size and density of nanoparticles and their embedding substrates, on the formation of CNTs.

**3:45 PM I11.8**

**LARGE SCALE SYNTHESIS OF NANOTUBES AND ONIONS BY ARC DISCHARGE IN LIQUIDS.** Manish Chhowalla, Noriaki Sano, Haolan Wang, Ioannis Alexandrou and Gehan Amaratunga, Cambridge University, Engineering Dept, Cambridge, UNITED KINGDOM.

Carbon nanotubes and fullerenes have extraordinary electrical and mechanical properties that make them ideal for numerous applications. However, for applications such as fuel cell electrodes and nano-composite structural materials, large quantities (kilograms) of the material are desired. The widely used methods to fabricate nano-materials require vacuum systems to generate plasmas using an arc discharge, laser ablation or glow discharge. These methods suffer in bulk production from not only the high investment and running costs of the vacuum equipment but also from low yield of the desired products. Furthermore, in addition to the desired nano-materials, the vacuum processes also yield unwanted contaminants (amorphous carbon and disordered nano-particles) so that a time consuming and costly purification step must be carried out. A simple method to fabricate high-quality spherical nano-materials in large quantities without the use of vacuum equipment is reported. The nano-particles are generated by an arc discharge between two electrodes submerged in water. Using this simple technique, we are able to generate spherical carbon onions with C<sub>60</sub> cores along with larger onion-like nested particles. In addition to carbon materials, we have also used this method to generate MoS<sub>2</sub> nano-particles. Our method requires only a dc power supply, carbon cathode and a consumable anode of the desired material and de-ionized water or liquid nitrogen. This method is outstandingly simple and economical compared to conventional techniques used to generate fullerenes and nanotubes.

**4:00 PM I11.9**

**MACROSCOPIC NEAT SINGLE WALL CARBON NANOTUBE FIBERS.** Lars M. Ericson, Sivarajan Ramesh, Joseph Sulpizio, Hua Fan, Rajesh Saini, Virginia A. Davis, Nicholas Parra-Vasquez, Jason Longoria, Carter Kittrell, Matteo Pasquali, Robert H. Hauge, Richard E. Smalley, Center for Nanoscale Science and Technology, Rice University, TX; Juraj Vavro and John E. Fischer, Materials Science & Engineering, University of Pennsylvania, PA.

Measured and predicted properties of single wall carbon nanotubes (SWNT) suggest that neat SWNT fibers will exhibit a variety of exceptional properties. Macroscopic fibers composed entirely of single wall carbon nanotubes have been successfully created. HiPco SWNTs were dispersed in strong acids at high concentrations (8-15 wt%) using high performance static mixing and extruded in a method that took advantage of the notable shear-thinning behavior of the SWNT/strong acid dispersion. Various extrusion and annealing conditions were explored. The fibers exhibit remarkable internal alignment, electrical properties, and mechanical properties.

**4:15 PM I11.10**

**MECHANICAL BEHAVIOR OF CERAMIC COATINGS REINFORCED WITH CARBON NANOTUBES.** Zhenhai Xia, Brian W. Sheldon, W.A. Curtin, J. Xu, and B. Chang, Division of

Engineering, Brown University, Providence, RI; Laura Riester, Metals and Ceramics Division, Oak Ridge National Lab, Oak Ridge, TN.

Carbon nanotube (CNT) reinforced composites have been touted to possess superb mechanical properties due to the unique structure and properties of carbon nanotubes, but no such materials have been fabricated or reliably tested to date. Here, we present the first results on the mechanical properties of highly-ordered CNT-reinforced ceramic matrix composites. The nanocomposites were produced by the template approach, in which CNT are deposited into a porous alumina matrix formed by anodization of aluminum, and are in the form of 20 micron thick coatings on an aluminum substrate. Nanoindentation tests were performed on surfaces both parallel and perpendicular to the longitudinal CNT axis. Indentation marks and associated damage were observed by SEM. Indentation parallel to the CNT axis induced cracks that intersect and deflect at the matrix/CNT interface, indicating interfacial debonding. Indentation perpendicular to the CNT axis induced cracks that show preliminary evidence of nanotube bridging. Indentation at high loads to cause chipping exposed fracture surfaces that exhibit CNT pullout. All of these phenomena indicate that these nanotube composites may function as tough materials. Nanocomposite modulus data obtained from indentation unloading curves were used along with analytic and finite element models to derive the Young's modulus of the porous Al<sub>2</sub>O<sub>3</sub> matrix (150 GPa) and the CNT (300 GPa) parallel to the nanotube axis; the latter values are much lower than typical estimates of CNT stiffness. The fracture toughness for cracking transverse to the CNT (typically a weak direction in CMCs) is estimated to be 7.4 MPa / m, comparable to tough engineered ceramics and much higher than that of bulk amorphous alumina.

**4:30 PM I11.11**

**MULTIFUNCTIONAL STRUCTURAL REINFORCEMENT FEATURING CARBON NANOTUBE FILMS.** Eric A. Lass, Rensselaer Polytechnic Institute, Dept. of MS&E, Troy, NY; Nikhil A. Koratkar, Rensselaer Polytechnic Institute, Dept. of Aerospace Engineering, Troy, NY; Bingqiang Wei and Pulickel M. Ajayan, Rensselaer Polytechnic Institute, Dept. of MS&E, Troy, NY.

High structural damping is an important design parameter for a wide variety of structural components and machine-elements. Conventional damping materials are polymers, and show promise for energy dissipation; however structural integrity issues associated with integration into composite/heterogeneous systems presents significant challenges. Also, these polymers cannot be used to reinforce the stiffness/strength of the composite structure. In order to overcome these limitations, there is a need to explore novel materials for structural damping and stiffness augmentation in composite systems. Recent theoretical and experimental studies have indicated that carbon nanotubes with their nanoscale dimension, high aspect ratio, and off-axis elasticity, provide an umbrella of ideal properties for application to engineering systems. Such nano-engineered materials are particularly attractive for structural reinforcement because they could potentially be seamlessly integrated within composite systems and offer the promise of multi-functionality in terms of improved damping, stiffness, strength, and fracture toughness. Multiwalled carbon nanotube thin films were fabricated using catalytic chemical vapor deposition of a xylene/ferrocene mixture. The resulting nanotube films were employed as inter-layers within composite systems to reinforce the interfaces between composite plies, enhancing laminate stiffness as well as structural damping. Experiments conducted using a piezo-silica composite beam with an embedded nano/adhesive film sub-layer indicated up to 200% increase in the inherent damping level and 30% increase in the baseline bending stiffness with minimal increase in structural weight. Scanning Electron Microscopy (SEM) characterization of the nano-film was also conducted to investigate the mechanics of stiffness and damping augmentation. The study revealed a fascinating network of densely packed, highly interlinked multiwalled nanotubes (MWNTs). This inter-tube connectivity resulted in strong interactions between adjacent nanotube clusters as they shear relative to each other causing energy dissipation within the nano/adhesive film. The cross-links between nanotubes also served to improve load transfer within the network resulting in improved stiffness properties.

**SESSION I12: POSTER SESSION**

Thursday Evening, December 5, 2002

8:00 PM

Exhibition Hall D (Hynes)

**I12.1**

**SIMULATION OF CARBON NANOTUBE PULL-OUT WHEN BONDED INTO A POLYMER MATRIX.** S.J.V. Frankland, V.M. Harik, ICASE, NASA Langley Research Center, Hampton, VA.

Molecular dynamics simulations of a carbon nanotube pulling through a polymer matrix are carried out and analyzed with respect to shear yield strength of the polymer-nanotube interface and the ensuing slippage of the nanotube relative to the polymer. Comparison is made of the behavior of non-bonded and functionalized composites during yield and slippage. Functionalization increases the shear yield strength relative to the matrix, and induces other failure mechanisms of the composite. The interfacial sliding is characterized in terms of an analog of Newton's friction law which is parametrized from the MD, and involves determining the viscosity at the interface.

#### **I12.2** Transferred to I10.9

#### **I12.3** A STUDY OF HYDROGEN ADSORPTION IN PRETREATED NANOCARBON. Sang Moon Lee, Japan Fine Ceramics Center, FCT Lab., Tsukuba, JAPAN; Satoshi Ohshima, Kunio Uchida, and Motoo Yumura, Research Center for Advanced Carbon Materials, AIST Tsukuba Central 5, Tsukuba, JAPAN.

On-board hydrogen storage is an important non-polluting technology being investigated as a potential substitute for petroleum-based fuels. However, the storage and transportation of hydrogen are still serious problems, resulting in the limitation of applications. Recently, it has been reported that carbon materials could adsorb a great deal of hydrogen. Here, multi-walled carbon nanotubes and metal-carbon composite nanoparticles are investigated. Hydrogen adsorption studies were performed using a gravimetric method in which weight changes in samples with gas adsorption were measured using a balance. In this study, a magnetic suspension balance (Mettler AT 261, resolution 0.01mg) was used. The thermal treatment was applied with carbon dioxide, oxygen, and steam for the development of a porous structure. The thermal treatment temperature was increased to 1173K at a rate of 293K/min and maintained for the proper time in an oxygenate atmosphere. Since there is considerable interest in understanding the surface and porous properties of nanocarbon, we have been investigating the adsorption of nitrogen on such nanocarbon. We have measured the adsorption isotherms of nitrogen on well-characterized nanocarbon. A comparison of samples before and after heat treatment was made. In addition, transmission electron microscopy was used to investigate the total structure. We will discuss the influence of thermal treatment of nanocarbon in an oxygenate atmosphere on the pore structure and adsorption of hydrogen.

#### **I12.4** AN APPROACH TO NANOGLASSES THROUGH ANODIC OXIDATION OF SPUTTERED ALUMINUM ON GLASS SURFACE. Satoru Inoue, Song-Zhu Chu, and Kenji Wada, National Institute for Materials Science, Advanced Materials Laboratory, Tsukuba, Ibaraki, JAPAN.

The new processes for the preparation of nanoglasses have been developed through anodic oxidation. The aluminum thin film sputtered on the ITO thin film on the glass surface was decomposed into alumina by anodic oxidation technique. The alumina layer possessed nanometer size pore array standing on the glass surface. The size of the pore was widened by acid etching from 10~20nm to a few hundred nm. The glass substrate having the alumina nanostructures on the surface could transmit about 80% of UV and visible light at the wavelength range of 200nm~800nm. The TiO<sub>2</sub> sol was impregnated into the pores of alumina layer and the sample was heated at ~400°C for 2 hr, converted into TiO<sub>2</sub> nanotubes of anatase phase. The acid etching could remove the alumina wall of the pores, leaving the titania nanotube array on the glass surface. These glasses were transparent to the light in UV-visible region. The electro deposition technique was applied to the introduction of nickel metal into pores, giving nickel nanorod array on the glass surface. The glass samples possessing titania nanotube array showed good catalytic function on the decomposition of acetaldehyde gas under the irradiation of UV light. The effect of the dimensions of the nickel nanorods on the magnetization was investigated.

#### **I12.5** ELECTROSTATIC PRODUCTION OF NANOFIBERS (ELECTROSPINNING): WHIPPING INSTABILITY AND THE FIBER DIAMETER. Sergey V. Fridrikh<sup>a</sup>, Jian H. Yu<sup>a</sup>, Michael P. Brenner<sup>b</sup>, and Gregory C. Rutledge<sup>a</sup>; <sup>a</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA; <sup>b</sup>Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA.

Electrospinning is a method of producing submicron (nano-) fibers by the stretching of a polymer solution jet in an external electric field. Due to combined action of surface tension, charge relaxation, and the repulsion of the surface charges, the jet undergoes a set of electrohydrodynamic instabilities. The varicose instability causes the

jet to break into the drops, while the whipping instability is responsible for the strong stretching of the jet and for the formation of nanofibers.

The potential applications of nanofibers are numerous. Their high surface area makes them an attractive candidate for filtering and absorbing applications. Due to their small diameter nanofibers may be used as a component in various composite materials. Non-wovens electrospun from biocompatible materials may be used for wound dressing and artificial tissue scaffolding. The first experimental accounts of successful applications of nanofibers as tissue scaffolds have emerged in the literature.

We developed a model giving quantitative predictions for the final diameter of the whipping jet. The final diameter of the jet (fiber) is set by the balance of surface tension and electrostatic repulsion of the surface charges. The simple analytical expression for the final diameter as a function of the surface tension, flow rate and electric current only is derived. For the most of fluids studied experimentally, it gives an estimated fiber diameter of about 1μm in agreement with published experimental data. Our experimental data on diameters of PCL fibers electrospun from methanol + chloroform solution show good agreement with theoretical predictions over a rather broad range of fiber diameters.

We also present numerical simulations and analytic formulae demonstrating both the whipping of the centerline of the jet, coupled to the thinning of the fiber diameter as it advects downstream. Predictions for the envelope of the whipping jet and the diameter of the jet as it changes along the jet's contour are presented. The experiments for testing these predictions are currently on the way. Accurate prediction of the fiber diameters and identification of how this diameter depends on experimental properties opens the door for inventing novel ways of controlling the fiber diameter.

#### **I12.6** Abstract Withdrawn.

#### **I12.7** DETECTION OF FREE VOLUME IN NANOCRYSTALLINE MATERIALS: EXPERIMENT VERSUS COMPUTER SIMULATIONS. Steven Van Petegem, Danny Segers, Ghent University, Dept of Subatomic and Radiation Physics, Ghent, BELGIUM; Helena Van Swyghoven, Florian Dalla Torre, PSI, GFA/ASQ, Villigen, SWITZERLAND; and Jan Kuripach, Charles University, Dept of Low Temperature Physics, Prague, CZECH REPUBLIC.

The excess free volume present in grain boundaries and triple junctions of nanocrystalline metals and alloys play a key role in the mechanical properties. It is well known that for instance open pores in samples synthesized by compaction are the reason for the lack of plasticity in these samples. Positron annihilation spectroscopy has been successfully applied in the study of the free volume distribution in nanocrystalline metals. Different types of defects such as vacancies and nanovoids could be identified. Were these free volumes are located and what their influence is on the mechanical properties is still an open question. Here we present the results of positron lifetime measurements performed on Ni and Ni<sub>3</sub>Al synthesized with three different methods: inert gas condensation, electrodeposition and high pressure torsion. Furthermore we present a new method to perform positron lifetime calculations in computer-generated nanocrystalline samples. Lifetime calculations are conventionally used to associate the lifetime of a positron with one certain modelled defect in order to interpret results from positron lifetime experiments. We have adapted this technique so it can be used in nanocrystalline materials having up to 10<sup>6</sup> atoms and several hundreds of free volumes. A comparison is made between the experimental and the computer-generated samples.

#### **I12.8** GROWTH OF CARBON NANOFIBERS ON ELECTROLESS Ni-P ALLOY CATALYST. T.K. Tsai, W.L. Liu, S.H. Hsieh, and W.J. Chen, Dept of Materials Science and Engineering, National Hsuwei Institute of Technology, Yunlin, TAIWAN.

Carbon nanofibers (CNFs) were grown on Ni-P alloy catalyst deposited on silicon substrate in a microwave heating chemical vapor deposition (CVD) system with methane gas at 650 J. The Ni-P alloy catalyst film with various thicknesses was plated by electroless plating nickel technique. The clustered surface of Ni-P alloy catalyst film directly provided the nucleation site for CNFs without any pretreatment before growth of CNFs. The CNFs grown on Ni-P alloy catalyst showed random orientation and composed of truncated and parallel graphite planes with defect tilted from their axis. Field emission measurement indicated the Ni-P catalyzed-CNFs exhibited excellent field emission properties. The diameter, growth rate and field emission properties show a strong correlation with the thickness of Ni-P alloy catalyst film.

### I12.9

MATERIAL PROPERTIES AND PROCESS COMPATIBILITY OF SPIN-ON NANO-FOAMED POLYBENZOXAZOLE FOR COPPER DAMASCENE PROCESS. Takashi Enoki, Kenzo Maejima, Hidenori Saito, and Akifumi Katsumura, Fundamental Research Laboratory, Research Department, Sumitomo Bakelite Co., Ltd., Kanagawa, JAPAN.

In shrinking dimensions of future semi-conductor devices, lower dielectric constant ( $k$ ) material is strongly required in Cu/low- $k$  damascene structure. According to the International Technology Roadmap for Semiconductors (ITRS) 2001, ultra low- $k$  interlayer dielectric materials ( $k < 2.4$ ) will be needed around 2005. Because the  $k$  value of air is one, nanofoaming with air is possible solution to provide lower  $k$  material. Polybenzoxazole is one of excellent heat resistant polymers and is synthesized via cyclization of its precursor (poly( $\omega$ -hydroxy)amide) by polycondensation between bis- $\omega$ -amino-phenol and dicarboxylic acid derivative monomers. The precursor shows good solubility to several organic solvents, which allows us spin-on application. Once the polybenzoxazole is obtained by cyclization from spin-on precursor by heat, it becomes insoluble and shows high thermal stability. We have designed a spin-on nano-foamed OxD (Oxazole Dielectrics) by taking advantage of polybenzoxazole chemistry considering nano-foaming process. In this presentation, we will report material and process properties of nano-foamed OxD ( $k=2.2$ , pore size  $<10$  nm suggested by SEM micrograph of its cross-section) which are important to consider Cu damascene process. We will discuss mechanical properties, thermal stability, process compatibility such as etching property, chemical stability and so on.

### I12.10

FERROMAGNETIC SHAPE MEMORY OF NANOSTRUCTURE Fe-Pd ALLOY. Teiko Okazaki, Takeshi Kubota, Yasubumi Furuya, Setuo Kajiwara<sup>a</sup> and Takehiko Kikuchi<sup>a</sup>, Faculty of Science and Technology, Hirosaki University, Hirosaki, JAPAN. <sup>a</sup>National Institute for Materials Science, Tsukuba, JAPAN.

Ferromagnetic shape memory Fe- 29.6 at%Pd alloy ribbon (about 60  $\mu$ m thickness) prepared by the rapid solidification, melt-spinning method, has a large magnetostriction of  $1.1 \times 10^{-3}$  when an magnetic field of 10 kOe is applied normal to the ribbon surface at room temperature. The magnetostriction of this ribbon is 10 times as large as polycrystalline bulk value before. The strain is caused by the conversion of variants in the martensite phase and depends strongly on a direction of applied magnetic field  $H$ , i.e., is maximized at  $H$  parallel to the thickness direction of ribbon. The magnetostriction increases with temperature and has maximum at phase transformation temperature, 380-400 K. However, the mechanically shape recovery effect of the ribbon has two-step phase transformation temperature of 300-330 K and 380-420 K. To investigate the origin, we observed the texture by using laser microscope and high resolution electronic microscope. The cross-section of ribbon shows columnar structure of about 10  $\mu$ m in width. The ribbon consists of three parts: both upper and bottom surfaces have smaller grains than 2  $\mu$ m with strong [100] texture and inner part has fine layer-structures of 30-40 nm thickness in grains. It can be concluded that this nano-scale composite structure makes phase transformation temperature increase from 300 K in surface to 380-400 K in inner part.

### I12.11

BONE-SHAPE NANOMATERIALS FOR NANOCOMPOSITES APPLICATION. Terry Xu and Rod Ruoff, Department of Mechanical Engineering, Northwestern University, Evanston, IL.

The template synthesis of bone-shaped nanostructures is reported. Porous anodic alumina (PAA) films with bone-shaped nanochannels are used as the template. The PAA films were prepared by a two-step anodization of aluminum. The material of interest, such as carbon, is chemical vapor deposited from gas-phase precursors such as ethylene to form the bone-shaped carbon nanotubes or nanorods. These novel bone-shaped nanostructures appear to be promising in nanocomposites applications, because the enlarged fiber ends may improve the mechanical interlocking between the matrix/nanostructure interface, perhaps leading to more effective load transfer.

### I12.12

NOVEL NANOSTRUCTURES FOR POTENTIAL INTEGRATION IN NANOCOMPOSITES. Terry Xu and Rod Ruoff, Dept of Mechanical Engineering, Northwestern University, Evanston, IL.

Nanosphere arrays (NSA) of polystyrene spheres were prepared on Si wafer substrates. Carbon was vapor deposited, and the NSA removed by sonication in water. The resulting C nanostructures have been characterized with AFM, SEM, and TEM. The quasi-periodic array of nanostructures (periodic over lengths of about 10  $\mu$ m) could find use in fundamental studies of nanocomposites and also in such

applications as field emission devices for flat panel displays, as will be briefly presented.

### I12.13

NEGATIVE PHOTORESIST BASED ON AN ACRYLATED POLY(ARYLENE ETHER). Timothy P. Bender, Richard A. Burt, Marko Saban, Paul F. Smith, Nancy Stoffel, Timothy Fuller, and Daniel Foucher, Xerox Research Centre of Canada, Mississauga, Ontario, CANADA.

A new photoresist material has been developed by our research group based on a poly(arylene ether) base resin. The material is made via a three step synthesis starting by reaction of 4,4-difluorobenzophenone with bisphenol-A in the presence of an endcapping agent to form a low molecular weight ( $M_w$  14,000 amu) narrow dispersed poly(arylene ether) base resin. This base resin is then chloromethylated and acrylated to form the final material. The degree of acrylation can be chemically controlled in order to control the crosslink density. This material can be formulated into a photoresist solution by dissolution in a variety of solvents and addition of appropriate initiators. This photoresist has several advantages over polyimide photoresist, namely an improved aspect ratio and reduced shrinkage after curing. This presentation will focus on the optimization of the synthesis of this material at a pilot plant scale as well as a discussion of the formulation of this material and its final application as a resist for ink jet print head application.

### I12.14

IMPACT MODIFICATION OF NANOCOMPOSITES WITH AN EPOXY MATRIX. Isil Isik, Ulku Yilmazer, and Goknur Bayram, Department of Chemical Engineering, Middle East Technical University, Ankara, TURKEY.

In this study, nanocomposites were synthesized using an epoxy resin as the matrix and organically modified montmorillonite as the reinforcing agent. Polyether polyol was added at various contents to improve the toughness of the nanocomposites. Triethylenetetramine was used as the curing agent. The morphology of the composites was characterized by X-ray diffraction and scanning electron microscopy. The mechanical behavior of the nanocomposites was evaluated in terms of impact strength, and tensile and flexural properties at different impact modifier and montmorillonite contents. The glass transition temperature ( $T_g$ ) was measured using a differential scanning calorimeter. X-ray diffraction pattern of nanocomposites showed that interlayer spacing of the modified montmorillonite expanded from 1.97 nm to approximately 3.8 nm, indicating intercalation during the preparation of the nanocomposite. Interlayer spacing of the intercalated clay did not change with respect to the impact modifier content. From the SEM micrographs of the nanocomposites, three distinct phases were observed: The epoxy-hardener matrix, the nonintercalated montmorillonite, and the polyether polyol phase as spherical domains. As the weight percentage of polyether polyol increased, the average diameter of the spherical polyol domains also increased. In samples with 1% weight impact modifier, a layered epoxy-hardener matrix structure was observed. The mechanical tests indicated that, in general, montmorillonite increased the modulus, but decreased the strength and strain at break in the 0-5% montmorillonite range. With respect to the impact modifier content, modulus and strength showed a maximum, the impact strength and  $T_g$  increased, but the strain at break decreased. Optimum properties were obtained at approximately 1% impact modifier and 3% montmorillonite content combination.

### I12.15

NANOCOMPOSITES WITH EPOXY MATRIX. Cigdem Basara, Ulku Yilmazer, Goknur Bayram, Middle East Technical University, Dept of Chemical Engineering, Ankara, TURKEY.

Epoxy-clay nanocomposites were synthesized to examine the effects of the content and type of different clays on the structure and properties of the nanocomposites. Diglycidyl ether of bisphenol-A (epoxy) was reinforced by 1-11 weight % Cloisite  $Na^+$  and Cloisite 30 B (Southern Clay Products) types of montmorillonite. Triethylenetetramine was used as the hardener. Cloisite  $Na^+$  is natural montmorillonite, Cloisite 30 B is organically modified and has suitable polarity to be used with the epoxy-hardener system. SEM results showed that as the clay content increased larger agglomerates of clay were present. Nanocomposites with Cloisite 30 B exhibited better dispersion and lower degree of agglomeration than nanocomposites with Cloisite  $Na^+$ . X-Ray diffraction patterns indicated that the interlayer spacing expanded from 11.7  $\text{\AA}$  to 38.1  $\text{\AA}$  in nanocomposites with unmodified clay and from 19.7  $\text{\AA}$  to 38.6  $\text{\AA}$  in nanocomposites with modified clay. Relative diffraction intensity was higher in nanocomposites with organically modified clay indicating a higher degree of intercalation in these nanocomposites as compared to nanocomposites with Cloisite  $Na^+$ . Also, as clay loading increased, the relative intensity increased up to 5 weight % clay. The glass transition values increased from

73°C, in the unfilled epoxy resin, to 83°C in the composite with 7 weight % organically modified montmorillonite. The tensile strength, tensile strain at break and impact strength values exhibited maxima at 1 weight % of modified clay loading. Adding 1 weight % organically modified clay improved the impact strength of the epoxy resin by 90.3%; in contrast, 1 weight % unmodified clay improved the impact strength by 29%. Tensile and flexural modulus increased, whereas the flexural strength and flexural strain at break decreased with increasing clay loading.

#### I12.16

**RHEOLOGY & PHASE BEHAVIOR OF SINGLE WALL CARBON NANOTUBES IN STRONG ACIDS.** V.A. Davis, L.E. Ericson, R. Sivarajan, R.K. Saini, C. Kittrell, W.E. Billups, R.H. Hauge, R.E. Smalley, and M. Pasquali, Rice University, Houston, TX.

Solutions of single wall carbon nanotubes (SWNTs) in strong acids are of interest for producing high performance neat SWNT fibers. We are measuring the rheological properties of solutions of SWNTs in 100% sulfuric acid and studying how they depend on SWNT concentration and temperature. Dynamic, steady shear rate and transient response data are providing insights into the phase behavior of SWNT / acid solutions. Concurrent optical microscopy is providing invaluable information on the phase diagram and on the structures formed in solution. Evidence so far from microscopy and rheology shows important similarities between SWNT / acid solutions and other solutions of rigid rod polymers used for producing high performance fibers such as Kevlar.

#### I12.17

**STOICHIOMETRY, CRYSTALLINITY, AND NANO-STRUCTURED MORPHOLOGY OF A FUNCTIONALLY GRADED APATITE ON Ti-AL-V.** J.D. Long, Ken Ostrivok, Shuyan Xu, Advanced Materials and Nanostructures Laboratory, Natural Sciences, Nanyang Technological University, SINGAPORE; and Valeri Ligatchev, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE.

This work reports on the successful fabrication of a biocompatible CaP-based bio-ceramic on bioinert Ti-6Al-4V orthopaedic alloy using a 13.56 MHz Plasma-Assisted RF Magnetron Sputtering Facility. The RF discharges were sustained in Ar/H<sub>2</sub>O with 600-800 W RF powers in the pressure range below 100 mTorr. Two different, Ti and hydroxyapatite solid targets were sputtered concurrently onto a negatively biased Ti-6Al-4V substrate. Each layer in the biocompatible coating does reflect certain functionality and has been investigated by cross-sectional FE-SEM imaging, XRD, and XPS analysis. The bottom layer, facing the metal alloy, is made of Ca-P based bio-ceramic with elevated concentrations of Ti, and is aimed at improving adhesion of the interlayer to the implant material, as well as the ceramic-metal interfacial stability. Significant improvement of the latter has been confirmed by the micro-scratch test. The middle layer is designed to simulate bone replacement cement and contains predominately calcium phosphate. In this layer, the stoichiometry and crystallinity of the CaP-based ceramic is an issue, to successfully reproduce the natural bone apatite. The XPS data show that this layer is composed of O, Ca, P and Ti, and reveal the formation of O=P groups and hybridization of O-Ca-P. The XRD pattern shows that the deposited films are composed of nano-crystalline calcium oxide phosphate with the preferred orientation varying with the processing parameters. Variation of the film deposition parameters is also instrumental in achieving various Ca/P ratios, intrinsic for a number of natural apatites. The outer, a few to few tens of nanometers thick, layer, requires special tailoring of the surface morphology in view of the optimized bio-molecule/protein attachment. The results of the atomic force microscopy reveal the optimized deposition conditions for the best nano-scaled roughness, homogeneity, island 'sharpness', inter-island 'valley' spacing, and 'valley' surface area for improved protein attachment, and hence, bio-compatibility. Preliminary cell culturing tests confirm the link between the tailored nano-scale surface morphology and biocompatibility.

#### I12.18

**HOT-PRESSING OF ALUMINUM-BASED ALLOYS PRODUCED BY MECHANICAL ALLOYING.** Vera Lúcia Arantes, Kátia Regina Cardoso, IP&D, Universidade do Vale do Paraíba, São José dos Campos, BRAZIL; and Carlos Alberto Cairo, Centro Tecnológico da Aeronáutica, São José dos Campos, BRAZIL.

The process of mechanical alloying, developed initially for production of nickel-based alloys hardened by oxides dispersion, have been very adequate for development of new materials and alloys. It allows the production of alloys formed by immiscible elements or with a high difference between melting temperatures. Furthermore, this technique allows obtaining nanomaterials, which has revolutionized the basic materials science and improved mechanical and magnetic properties of metallic alloys. This work focused on the utilization of hot-pressing as

a process of consolidating mechanical alloyed aluminum alloys, with addition of titanium and magnesium for use in high temperatures. Hardened aluminum alloys with dispersion of intermetallic were developed by mechanical alloying, with fine grains and based upon commercial compositions with addition of elements with low solid solubility in aluminum and capable of forming intermetallics stable up to elevated temperatures. The powders obtained and the hot-pressed final samples were characterized by X-Rays diffraction, Differential Scanning Calorimetry and electronic microscopy.

#### I12.19

**INORGANIC-ORGANIC HYBRID MATERIALS: SAXS INVESTIGATIONS OF METAL-OXIDE NANOCLUSTERS IN AN ORGANIC POLYMER MATRIX.** Viktoria Torma, Silvia Gross, Nicola Husing, U. Schubert, Technische Universität Wien, Institut für Materialchemie, Wien, AUSTRIA; Herwig Peterlik, Universität Wien, Institut für Materialphysik, Wien, AUSTRIA; and Peter Fratzl, Erich Schmid Institut der Österreichischen Akademie der Wissenschaften & Montanuniversität Leoben, Leoben, AUSTRIA.

Surface modified metal clusters such as  $Ti(4)O_2(OEt)_8(OMc)_8$  [1],  $Zr(4)O_2(OMc)_12$  [2],  $Ta(4)O_4(OEt)_8(OMc)_4$  [3], or  $Hf(4)O_4(OMc)_12$  ( $OMc$  = methacrylate) can be synthesized by controlled hydrolysis of the methacrylate-substituted metal alkoxides. Because the ligand shell of the clusters is substituted by reactive ligands like acrylate or methacrylate, the new clusters can be polymerized by a radical polymerisation reaction into organic polymers. The cluster crosslinks improve the mechanical properties and the thermal stability of the organic polymer significantly. The aim of this work was to obtain information about the arrangement of the clusters in the organic polymer matrix from Small Angle X-ray Scattering (SAXS). It has been shown in previous work [1,3] that polymerization of clusters with small structural differences, such as  $Ti(4)O_2(OEt)_8(OAc)_6$  and  $Ti(6)O_4(OEt)_8(OMc)_8$ , results in materials with somewhat different properties. By means of SAXS the structural reasons of these differences can be investigated like agglomeration of the clusters or homogeneous distribution. [1] B. Moraru, N. Husing, G. Kickelbick, U. Schubert, P. Fratzl, H. Peterlik, *Chem. Mater.*, **14**, 2732 (2002) [2] G. Trimmel, S. Gross, G. Kickelbick, U. Schubert, *Appl. Organomet. Chem.*, **15**, 401 (2001) [3] S. Gross, V. Di Noto, G. Kickelbick, U. Schubert, *Mat. Res. Symp. Proc.*, **726**, in press.

#### I12.20

**HOT SUPERPLASTIC POWDER FORGING OF BULK NANOCRYSTALLINE CERAMICS.** Adwaita Chaudhuri, Chiraporn Auechalitanukul and W. Roger Cannon, Rutgers University, Department of Ceramic and Materials Engineering, Piscataway, NJ.

Fabrication of bulk nanocrystalline zirconia-alumina by Hot Superplastic Powder Forging (HSPF) is reported here. Powders are rapidly quenched from a plasma torch to achieve a non-equilibrium microstructures. Annealing at temperatures in the range of 1200-1300°C nucleates and grows a nanocrystalline two-phase bi-continuous microstructure. Powders then are pressed in a small die in a dilatometer to obtain the stress and temperature dependence of densification. Results are compared with superplastic creep behavior.

#### I12.21

**PREFERRED ORIENTATION IN FIBERS OF HIPCO SINGLE WALL CARBON NANOTUBES FROM DIFFUSE X-RAY SCATTERING.** W. Zhou, K.I. Winey, J.E. Fischer, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA; S. Ramesh, R.K. Saini, L.M. Ericson, V.A. Davis, and R.E. Smalley, Center for Nanoscale Science and Technology, Rice University, Houston, TX.

Bulk samples of single wall carbon nanotubes produced by the HiPco process exhibit little or no Bragg intensity in x-ray scattering due to the poor crystallinity compared to arc and laser material [1]. Fibers produced from HiPco tubes, described elsewhere in this Symposium, offer promise for high strength, light weight, electrically conducting structural elements at lower cost than other nanotube forms. The mechanical properties of such fibers will depend on the degree of SWNT alignment induced by the processing [2]. Texture analysis based on 2D x-ray fiber diagrams is widely used to study crystalline materials. Here we study preferred orientation in non-crystalline HiPco SWNT fibers by analyzing the diffuse form-factor scattering from uncorrelated tubes. We obtain a mosaic FWHM from the azimuthal dependence of diffuse intensity summed over an appropriate Q range. We assume that some fraction of the nanotubes are aligned while the rest remain randomly oriented. The aligned part can be described by an orientation distribution function, while the other part is represented by a constant independent of azimuth. From 2D x-ray measurements we can accurately determine the FWHM of the distribution function for the aligned part. Also, by subtracting a contribution to diffuse scattering from porosity etc., we get a good

estimate of the unaligned fraction. We show how these two parameters vary with fiber processing variables. The x-ray results are confirmed by polarized Raman scattering. Results of this analysis can be used to optimize the fiber extrusion process. [1]. W. Zhou et al., *Chem. Phys. Lett.* 350, 6-10 (2001). [2]. R. Hagenmueller et al., *Chem. Phys. Lett.* 330, 219 (2000).

#### I12.22

**PREPARATION AND CHARACTERIZATION OF DOUBLE-WALL, FLATTENED MULTI-WALL AND COAXIAL-CABLE-LIKE CARBON NANOTUBES.** W.Z. Li, J.G. Wen, and Z.F. Ren, Boston College, Physics Department, Chestnut Hill, MA.

It is well known that the microstructure of carbon nanotubes determines their physical and electronic properties. Thermal CVD is a versatile method for growing carbon nanotubes with different structures. We will report our recent success on achieving double-wall, flattened multi-wall and coaxial-cable-like carbon nanotubes. The double-wall nanotubes (DWNTs) grow in the form of small bundles, and each bundle consists of several individual DWNTs with outer diameter of 2-3 nm. The extremely clean surface and inside channel together with the high graphitization make the DWNTs ideal both for investigating the interlayer interactions and for exploring the possible applications in nanoelectronics. The flattened multi-wall nanotubes are formed during the growth, indicating a different growth mechanism from that of cylindrical nanotubes. Theoretical and experiment studies have shown that structure deformation of the nanotubes will affect their electronic behavior; therefore, the realization of the pure flattened nanotubes may offer more opportunities for the development of nanoelectronic devices. Based on the analysis on the microstructures, the growth mechanism of flattened nanotubes will be discussed. In addition, the growth and structure of coaxial-cable-like nanotubes will be presented.

#### I12.23

**SYNTHESIS OF CARBON NANOTUBE WITH CONTROLLED NANOSTRUCTURE AND APPLICATION.** Wansoo Huh, Barry Farmer, Richard Vaia, Air Force Research Laboratory, MLBP, Wright-Patterson AFB, OH; and Don Shiffler, AFRL/DE, Kirtland AFB, NM.

There has been much effort devoted to the fabrication of carbon nanotube and it is well known that they can be made using several techniques. For the design and processing of nano-size devices and nanocomposite, the dimension control of carbon nanotube (diameter, thickness, and length) is required and expanded applications of carbon nanotube can be made. This study investigates the feasibility of producing carbon nanotubes with controllable dimensions and high aspect ratio for applications in nano-size devices and nanocomposites. Our approach is to devise a method of growing carbon nanotube using a catalyst deposited in an patterned array of pores. By varying the processing parameters, such as gas formulation, gas flow rate, temperature, structure of carbon nanotube can be controlled. The catalyst formulation for electrochemical deposition in the template and chemical formulation for the synthesis carbon nanotube in a thermal CVD process have been studied to obtain the desired dimensions of carbon nanotubes. The structural properties of synthesized carbon nanotubes have been characterized with relation to synthesis variables using various instrumental analysis methods, including Raman spectroscopy and TEM.

#### I12.24

**POLYMER-ATTACHED FUNCTIONAL INORGANIC-ORGANIC HYBRID NANOCOMPOSITE AEROGELS.** Xipeng Liu, Mingzhe Wang, and William M. Risen, Department of Chemistry, Brown University, Providence, RI.

Novel materials in which modified inorganic-organic hybrid silica aerogels are attached to polymer chains have been synthesized. The aerogels are based on chitosan, a biderived polymer from chitin, and contain silica and, in some cases, metal ions. The first stage of the modifications includes attachment of isocyanate, amine, and epoxy groups onto the chitosan chains embedded within the aerogel. These groups are employed in the second stage to "string" aerogel particles along functionalized linear polymers or to employ these polymers to crosslink the composite aerogels. The initial chitosan-silica aerogel particles have an ultimate particle size of about 2nm, and their functionally modified forms were reacted at sizes up to 100nm. They are of two chemical types; chitosan-silica, and metal-chitosan-silica with metal ions coordinated to the chitosan. These aerogels can take up and hold dyes and water-soluble drugs. In addition, analogous chemistry has been done with methacrylate-substituted metal-silica-chitosan aerogels and vinyl functionalized substrates. The chemical and physical characterization of these and new systems based on polymers from polyallylamine, and poly[dimethylsiloxane-co-(3-aminopropyl)methylsiloxane] to a range of vinyl alcohol copolymers will be presented.

#### I12.25

**NANOSCALE MODIFICATION OF THE SURFACE OXIDE OF GALLIUM ANTIMONIDE (GaSb) SUBSTRATES FOR DEVICE APPLICATIONS.** Xianglin Li, Bongwoo Kang, Maria Ospina, Xin Liu, Changmo Sung, Center for Advanced Materials, University of Massachusetts, Lowell, MA; William Goodhue, Department of Physics and Applied Physics, Photonics Center, University of Massachusetts, Lowell, MA; Lisa P. Allen, Tom G. Tetreault, Epion Corporation, Billerica, MA; and David Bliss, Air Force Research Laboratory/SNHC, Hanscom AFB, MA.

Gallium antimonide (GaSb) is an important substrate material as a platform for fabricating low-power high frequency heterostructure-based 0.61 nm devices. Providing high-quality GaSb substrates, however, is a challenge. In particular, producing a damage free surface with a designed surface oxide is difficult in this soft material using standard chemical-mechanical polishing (CMP) techniques. Recently, gas cluster ion beam (GCIB) processing, a nanoscale surface modification technique, has been used to smooth and remove surface and sub-surface damage from polished two-inch (100) GaSb wafers. In this work, the GCIB process is shown to be capable of forming uniform engineered oxides on the surfaces of CMP polished GaSb wafers. For example, the GCIB process is able to replace a CMP produced mixed gallium and antimony surface oxide with a uniform single-state gallium surface oxide. Control of the surface oxide along with polish damage removal and surface smoothing is expected to lead to a true high-yield GaSb "epi-ready" wafer. In this paper the GCIB recipes used in the work will be discussed. The surface oxides have been characterized by spectroscopic ellipsometry and x-ray photoelectron spectroscopy. Cross-sectional transmission electron microscopy and x-ray diffraction of the surface and sub-surface indicate that GaSb crystallinity is maintained with a reduction in the rocking curve FWHM (Full Width at Half Maximum) after GCIB etching and smoothing of the material surface.

#### I12.26

Abstract Withdrawn.

#### I12.27

Transferred to I4.2

#### I12.28

**NANOCOMPOSITE FIBERS.** Prabir Patra, Yong Kim, Armand Lewis, and Steven Warner, University of Massachusetts, Dartmouth, Dept of Textile Sciences, North Dartmouth, MA.

Nanocomposite fiber materials have been under research study for a number of years. The concept involves integrally dispersing nanosized particles of a second phase inorganic material into fiber forming polymer matrices such as nylon or polyester. The material goal here involves obtaining biphasic fibers with high mechanical stiffness and strength, electrical conductivity and/or enhanced other features such as dyeability. Thus far, the main difficulties toward achieving nanocomposite fibers are: (1) the inability of obtaining large quantities of nanoparticles in a pure un-agglomerated state, (2) the ability of obtaining a uniform, intimate dispersion of single entity nanoparticle in a fiber polymer matrix. We have approached these problems in the context of using carbon nanotube (CNT) materials and/or nanosilica particles as the impending polymer reinforcing species. Some success has been achieved in CNT-agglomerate disruption using electrostatic plasma treatments as well as the sonication of mixtures of CNTs in gum arabic solutions. In other work, a number of commercially available CNT/thermoplastic molding compounds have been used as CNT concentrates. These concentrates were suitable for blending with nylon 66, and polybutyleneterephthalate (PBT). While the melt blending of these compounds was successful, the extrusion of these materials into fibers was not. The CNT particles in the polymer matrix were too agglomerated. Other similar work, with nanosilica reinforced PET, enabled the fabrication of fibers from the melt. Here, measured fiber shrinkage peak forces were found to increase with an increase in nanosilica particle loading. This demonstrated the reinforcing effect of the silica particles. This observation appears to validate the hypothesis that a fiber can be reinforced by intimately blended inorganic nanoparticles.

#### I12.29

**SIMULATION OF MORPHOLOGY AND SURFACE VIBRATION IN COPPER AND GOLD NANOPARTICLES.** Yoshiaki Kogure, Yukie Kato, Tadatoshi Nozaki and Masao Doyama, Teikyo University of Science & Technology, Uenohara, Yamanashi, JAPAN.

Surface morphology and thermal vibration of atoms are closely related with the mechanical and thermal properties of nanoparticles. Formation and vibrational states in the nanoparticles at elevated temperatures are investigated by means of molecular dynamics simulation. The number of atoms in the particles is in the range of 1000 and 10000. The embedded atom method potentials for Cu and

subgrain rotation and coalescence forming coarse grains during the abnormal grain growth process were discussed.

#### 9:30 AM I13.3

**WEAR BEHAVIOR OF CrN BASED HARD PVD COATINGS DEPOSITED BY HIGH POWER PULSED MAGNETRON SPUTTERING AND COMBINED CATHODIC ARC/UNBALANCED MAGNETRON SPUTTERING TECHNIQUES.**  
A.P. Ehiasarian, P. Eh. Hovsepian, W.-D. Münz, Materials Research Institute, Sheffield Hallam University, Sheffield, UNITED KINGDOM; L. Hultman and U. Helmersson, Thin Film Physics Division, Department of Physics and Measurement Technology, Linköping University, Linköping, SWEDEN.

CrN thin films with low wear rates have been deposited by the novel high power-pulsed magnetron sputtering (HIPIMS) method, which utilizes peak power densities of typically 3000 Wcm<sup>-2</sup>. Sliding wear coefficients of  $2.3 \times 10^{-16}$  mN<sup>-1</sup> m<sup>-3</sup> have been measured in pin-on-disk tests against Al<sub>2</sub>O<sub>3</sub> ball under a load of 5 N. Unbalanced magnetron (UBM) sputtered CrN coatings tested under similar conditions exhibited wear coefficients increased by an order of magnitude, reaching a value of  $8.9 \times 10^{-15}$  mN<sup>-1</sup> m<sup>-3</sup>. Superlattice structured CrN/NbN (bi-layer thickness ~3.5 nm) coatings deposited by UBM sputtering were also inferior to HIPIMS CrN with wear coefficients in the range of  $3 \times 10^{-15}$  mN<sup>-1</sup> m<sup>-3</sup>. The voided columnar microstructure observed in transmission electron microscopy cross sections (XTEM) of the UBM deposited CrN films in combination with the low microhardness in the range of HK<sub>0.025</sub> = 2100 determined the lower wear resistance of these coatings. The multilayer structured CrN/NbN coatings had a higher hardness of HK<sub>0.025</sub> = 3500, however, when deposited at low bias voltages of U<sub>B</sub> = -75 V, the microstructure was predominantly columnar and voided. In contrast, the HIPIMS-deposited CrN coatings exhibited a dense microstructure and a high hardness of HK<sub>0.025</sub> = 2800. These properties result from the high plasma densities of  $10^{13}$  cm<sup>-3</sup> and the 30% ionized sputtered metal atoms found in the deposition flux produced by the HIPIMS technique. It could be speculated that the dense microstructure and strong bonding between the columnar grains of the film could make the overall coating more wear resistant. All UBM coatings had an excellent adhesion with scratch test critical load values, L<sub>C</sub>, in the range of 60 N while the HIPIMS CrN had L<sub>C</sub> = 85 N. The residual stress determined by X-ray diffraction analysis was -2 GPa for the UBM CrN, -1.5 GPa for the superlattice coating and -3.5 GPa for the HIPIMS CrN.

#### 9:45 AM I13.4

**PLASTIC RELAXATION MECHANISMS IN SYSTEMS WITH A TWIST-BONDED LAYER.** Catherine Priester UMR CNRS 8520/Dépt ISEN, Villejuif d'Asq, FRANCE and Geneviève Grenet, LEOM UMR CNRS 5512, Ecole Centrale de Lyon, Ecully, FRANCE.

We investigate here, from a theoretical point of view, how a compliant behavior can be reached in systems that present a bonded interface buried not too far from the surface. For this we consider systems with a twist bonded interface under a layer formed from two mismatched layers with a heterojunction in between, and study the motion of misfit dislocations in them. In such systems, threading dislocations at the end of moving edge dislocations appear to play a key role on the barriers for dislocations spreading into the sample, dislocations either introduced from the edge of the sample or nucleated in the sample core. Several dislocations are considered :

- usual edge dislocation located at the heterojunction, the threading dislocations being located in the strained layer
- usual edge dislocation located at the bonded interface, the threading dislocations being located in both twist bonded and strained layer
- a kinked-edged dislocation [1] located at the bonded interface, the threading dislocations being located in both twist bonded and strained layer
- a couple of edge dislocations, one being located at the heterojunction, the other at the bonded interface, the threading dislocations being limited in the twist bonded layer
- one edge dislocation at the heterointerface an a kinked edge dislocation at the bonding interface, the threading dislocations being limited in the twist bonded layer.

Comparison between the spreading curves of these different dislocations permit us to give new insights into the compliancy ability of such systems.

1:such kink-edge dislocations, first presented in S. Rohart, G. Grenet and C. Priester, Applied Surface Science 7518 (2001) 1, are specially well adapted to the strain field induced at the twist bonded interface.

#### 10:30 AM \*I13.5

**POLYMER NANOCOMPOSITES: MANUFACTURING, STRUCTURES, THERMAL AND MECHANICAL PROPERTIES.**  
Farzana Hussain, and Derrick Dean, Department of Mechanical Engineering and Center for Advanced Materials, Tuskegee University, Tuskegee, AL.

Layered silicates dispersed as a reinforcing phase in a polymer matrix are one of the most important forms of inorganic-organic nanocomposites, making them the subject of intense research. We have recently prepared several thermoset-based traditional and nanocomposites. These modified resins were also used to prepare fiber reinforced composites. Montmorillonite nano clay particles were incorporated into neat organic vinyl ester and SC-15 epoxy resin at different weight percentages (0.5%, 1%, 2%, 5% and 10%). The dispersion of clay particles into resin was carried out through mechanical stirrer and ultrasonic method. This paper is primarily focused in studying the effects of nano clay particles on improving mechanical and thermal properties of the polymer matrix composites. S2-glass/vinyl ester and S2 glass-epoxy nanocomposites were manufactured through an affordable vacuum assisted resin infusion method (VARIM). The results show significant improvements in mechanical and thermal properties of the nanostructured materials with low loading of organo silicates, which offer promise of economically improving the performance of the fiber reinforced composites. Thermal property measurement includes thermo gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Mechanical properties such as interlaminar shear strength, flexural strength, flexural modulus and fracture toughness of polymer matrix was improved in nano structured materials owing to their unique phase morphology and improved interfacial interactions. Optical and Scanning Electron Micrographs were taken to examine the failure surfaces. Molecular dispersion of the layered silicate within the cross-linked matrix was verified using Wide Angle X-Ray Diffraction (WAXD) and Transmission Electron Microscopy (TEM) revealing that intercalated nanocomposites were formed. TEM also indicated favorable interaction between the silicate clays and the glass fibers, which are also silicon based, indicative of enhanced matrix-fiber adhesion.

#### 11:00 AM **PANEL DISCUSSION**

**NANOMATERIALS AND NANOTECHNOLOGIES: A GLOBAL VIEW AND HOW TO ENHANCE INTERACTIONS AND APPLICATIONS.**